European Science Foundation Exploratory Workshop

Isotopic microsampling in Earth, Environmental and Archaeological Sciences

1. Executive Summary

Note that scientific abstracts, a list of participants, and a summary of the workshop findings are all available at the workshop website;
http://www.esf.dur.ac.uk/

a. Background and objectives

Isotope ratios in minerals are widely used in earth-, environmental-, and archeological science in order to unravel timescales of geological-, environmental-, and biological-processes contained within our solar system. Many of these can only be investigated using analytical techniques providing data at spatial resolutions well within the scale of minerals available for research.

The use of isotopic data as tracers in Earth, Environmental and Biological Sciences will enable us to determine the mechanisms and rates of natural processes, ranging from fish migration patterns and temperature change in the ocean to crystal growth in magmas. The need to explore these variations within natural materials at the smallest scale has been recognized for some time and investigations are underway to determine the degree of stable isotopic fractionation experimentally. Rapid spatially-resolved precise and accurate isotope determinations are potentially now possible through laser-ablation (LA) and multicollector-mass-spectrometry. However, while the capacity to produce isotopic data on a sub-mm scale from biological and environmental materials has been demonstrated, the ***validity*** of such data still remains a matter of question. In order to investigate any small scale variations in stable and radiogenic isotope ratios in natural or synthetic systems, reference materials with known isotopic homogeneity on the micro-scale are needed to determine the accuracy and precision of these measurements and to be used for standardization in the investigation of stable isotope systems. However, available solid isotopic reference materials (IRMM) with unknown micro-scale homogeneity cover only the elements Pt and Fe as metals, Li as carbonate and Si as oxide, while elements such as Mg, Ca, Sr and others are only available in form of solutions, therefore unusable for laser-ablation.

b. The workshop

The workshop was held at the University of Durham (Sept 8-11) to discuss these issues and offer possible solutions and

methodologies/protocols which would allow the community to use laser-ablation isotopic data with confidence. The workshop was attended by ~ 30 researchers from 10 countries across the EC – along with representatives from the USA and Australia. Most participants were from academic institutions, but participants from laser and mass spectrometer companies involved with developing the analytical technologies under discussion also attended. Three days of keynote talks were interspersed with equal-length discussion periods, led by one or more pre-prepared facilitators. Refreshment breaks allowed opportunities to view posters or tour the analytical facilities here at Durham. On two of the evenings formal events (icebreaker, workshop dinner) were scheduled to allow further informal discussion of many of the issues raised.

c. The outcome

A large number of factors can affect precision and accuracy – the laser wavelength used and operating conditions, the cell design and carrier gas, the ICP design and operating conditions. Participants agreed that

- Certain key parameters should always be measured and reported as routine in laser ablation analyses in order for us as a community to monitor and evaluate data quality
- Progress in the field of isotope ratio determination via laser ablation requires a concerted and coordinated effort to develop and characterize standard materials so that the effects of different experimental parameters can be constrained, and results from different laboratories can be reliably compared.

These issues are detailed further in section 3.

2. Scientific Content

The content over the three days comprised, as reflected in the scientific programme (section 4);
Methods and techniques I
Methods and techniques II
Applications

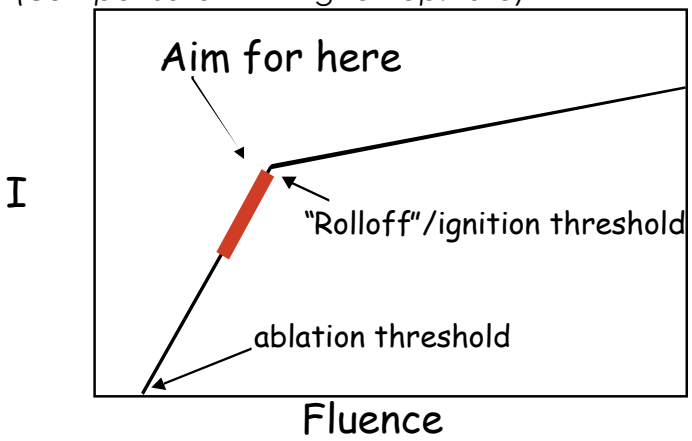
3. Assessment of the Results

There was general agreement that certain parameters can be optimized to improve performance. However, the unanimous message from the workshop was that we will never be able to compare laser-ablation isotopic data confidently on an inter-laboratory basis until we have well-characterised standards available. Therefore the full potential of laser-ablation ICPMS techniques to address major scientific issues cannot be presently realized.

The need to develop both protocols and standards in order to make progress with laser ablation analysis was discussed with ESF representatives who pointed out that the recent call for EUROCORES specified precisely the kinds of issues we have identified as areas of potential research. A group of participants has consequently forwarded a pre-proposal to the EUROCORES program. The following summary of important points was developed as a powerpoint file and placed on the workshop website;

1. Particle size distribution

- Use lower fluence to reduce condensation blankets
  - *(compensate with higher rep. rate)*



2. Robust plasma conditions

- Monitor using Th-U:
  - *Aim for Th/U (NIST Glass) 0.9-1.0*
  - *Aim for ThO <0.5-1%*

  (achieve by reducing gas flow)

3. Laser ablation strategies

- Low pit aspect ratios w>d
- Raster OK once surface cleaned
- Use wool filter or impactor (reduces signal by 10-15%)
- Use Al sampling cones with smaller orifice
- Optimise sample-skimmer cone distance
- Maximise pumping

4. Matrix-related calibration

- NIST glass works for silicates and carbonates (at least for elements)
- NIST glass may introduce memory effects - these can be monitored with Na

5. Standards

- We need them!

- Available:
  - *NIST glasses*
  - *USGS glasses*
- Needed
  - *Mineral standards*
  - *Sulphides*

6. What should we agree to report?

- Laser type
- At least one stable isotope ratio
- Fluence/ power
  - *(how do we measure this?)*
- Pulse width and rep. rate
- Ablation pit geometry
- Th/U and ThO

4. Final Program

Weds Sept 8th: evening Icebreaker
7.30pm Department of Earth Sciences (TR5 – 235)

Discussion Program:

- Talk presenters are urged not to over-run the talk time allocated. 10 minutes of question/ answer time is allowed at the end of each presentation.
- Posters will be displayed throughout the workshop
- All participants are welcome to use select AV materials (the odd overhead) to add to discussion

Thurs Sept 9th; Day 1: Methods and techniques I

Chairs/ Discussion leaders: Matt Horstwood

	Delegate	Talk Title/ activity
8.45 a.m.	ESF representative	Introduction to ESF activities and workshops
9.00 a.m.	Jon Davidson	Welcome and introduction
9.30 a.m.	Paul Mason/ Ingo Horn	LA-ICP-MS: some basics
10.15.a.m.		COFFEE
10.45.a.m.	Telouk Phillipe	Using laser ablation ICP-MS at 157 nm for isotopic ratios
11.30 a.m.		***Discussion – lasers and ablation cells; their role in producing precise and accurate data***
1 p.m.		LUNCH
2.15	Elburg Marlina	Assessing accuracy of Sr isotope measurements by LA-MC-ICP-MS
3.00	Mueller Wolfgang	Accurate and precise Sr and Hf analysis of geological and biological materials
3.45		COFFEE
4.15	Charlier Bruce	An overview of microdrilling and TIMS techniques for high-precision, high-accuracy in-situ Sr isotopic measurements in a range of silicate minerals.
5.00		***Discussion – evaluating data accuracy and precision***

Fri Sept 10th; Day 2: Methods and techniques II

Chairs/ Discussion Leaders: Paul Mason, Ingo Horn and Steve Eggins

	Delegate	Title
9.00 a.m.	Kosler Jan	Elemental and isotopic fractionation during laser ablation sampling
9.45 a.m.		COFFEE
10.15 a.m.	Horn Ingo	Defeating Elemental and Isotopic Fractionation - Experiments using UV - femtosecond LA-MC-ICP-MS
11.00	Bouman Claudia	Multi Ion counting ICPMS and TIMS: applications
11.45 p.m.		***Discussion – Dealing with Interferences and mass bias a)Elemental Fractionation b)Particle size related fractionation c) Zn/Cu in Brass, why it is different from above***
1.00		LUNCH
2.15	Bunce, Lucy	High throughput U-Pb age dating using current generation and next generation of multi-ion counting ICPMS; examples from a real lab.
3.00	Mason Paul	What are 'matrix effects' in laser ablations ICP-MS?
3.45		COFFEE
5.00		***Discussion – matrix effects on fractionation and accuracy***

7.00 p.m. Workshop dinner, Oldfields Restaurant, Durham

Sat Sept 11th; Day 3: Research applications and case studies

Chairs/Discussion leaders: Graham Pearson & Jon Davidson

	Delegate	Title
9.30 a.m.	Eggins Steve	Optimised compositional depth profiling and surface mapping - applications to the earth, environment and archaeological sciences.
10.15 a.m.		COFFEE
10.45 a.m.	Bendall Chris	Part 1: Pb and Cu isotopic analyses of ancient metal alloys by LA-MC-ICPMS. Part 2: S isotopic analyses of sulphides by LA-MC-ICPMS
11.30 a.m.	Heinin Kordula	Shade tolerance and nutrient status of fagus sylvatica and Acer pseudoplatanus
12.00 noon		LUNCH
1.00 p.m.	Conticelli Sandro	Trace element and Sr-isotope in situ analyses in minerals of volcanic rocks from Italian Provinces: tracers of petrogenic processes.
1.45 p.m.	Pearson Graham	Micro-analysis of individual sulphides for Re-Os isotopes:- applications to dating diamonds and other mantle events.
2.30 p.m.		COFFEE
2.45 p.m.	Chertkoff Darren	Sr isotopic studies at the mineral scale in volcanic rocks
3.45 p.m.		***Discussion – The need for standards. The future of in-situ microsampling Message to the ESF***
5.00 p.m.	ESF representative	Wrap-up

5. Final list of participants

Name	Contact	Age (where provided)	Country of Origin
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