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ISOTOPIC IMAGING OF MINERALS WITH NanoSIMS

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Matt Kilburn is currently Director of the Centre for Microscopy, Characterisation and Analysis, (CMCA) at the University of Western Australia (UWA). With a background in Earth Science, Matt holds a BSc in Planetary Science from University College London and a PhD in experimental petrology from the University of Bristol. After postdoctoral positions at the Max Planck Institute for Chemistry in Germany Matt joined the Department of Materials at Oxford University to develop the new NanoSIMS capability. In 2006, Matt moved to Australia to lead the Ion Probe Facility at UWA. The Facility currently houses three state-of-the-art ion microprobes: a CAMECA IMS 1280 and two CAMECA NanoSIMS 50L, making the CMCA one of the best-equipped SIMS facilities in the world. Matt's research revolves around developing SIMS applications for a wide range of disciplines, from biomedical research to materials science. He also works as a consultant to the International Atomic Energy Agency providing environmental analysis for nuclear safeguards.

ABSTRACT

SIMS is a highly versatile technique for the analysis of geological materials, combining *in situ* microbeam measurements with the high sensitivity and specificity of mass spectrometry. Most of the elements in the periodic table with a high dynamic range (allowing both major and trace element analysis simultaneously), but moreover, the mass spectrometry aspect allows the detection and quantification of individual isotopes. SIMS has long been used for in situ isotope measurements and is well-established as the gold-standard for U/Pb geochronology and stable isotope measurements in minerals such as zircon. NanoSIMS is a variant of SIMS that allows imaging with high sensitivity (sub-ppm) at high spatial resolution (~100 nm). Imaging trace elements and isotopes in minerals simultaneously can yield new insights into compositional changes resulting from diffusion, dissolution, radiation damage and biogenic controls.

1. *INTRODUCTION*

Secondary ion mass spectrometry (SIMS) is a highly versatile technique for the analysis of geological materials, combining *in situ* microbeam measurements with the high sensitivity and specificity of mass spectrometry [1]. SIMS is a surface analysis technique that uses a highly energetic ion beam to 'sputter' material from a sample surface, which is then analysed in a mass spectrometer. The primary ion beam impacts the sample surface causing a cascade-collision within the top few atomic layers, releasing material from the surface. The sputtered material consists of atoms, atom clusters, molecular fragments, and backscattered primary ions, and the small proportion of this material that is ionised (secondary ions) is extracted into a mass spectrometer using electrostatic fields. The amount of ionised material depends on a number of factors, including the chemical structure of the substrate, the ionisation efficiency of the elements within the substrate, and the nature and energy of the primary ion used. Dynamic-SIMS uses a high-energy beam that erodes the sample surface, producing a high secondary ion flux, but destroying the molecular bonds between the atoms in the sample. This results in the detection of elemental ions only (although some non-stoichiometric ion clusters are formed in the sputtering process). Dynamic-SIMS typically employs magnetic-sector mass analysers, in which secondary ions are deflected in a magnetic field depending on their mass to charge ratio, *m/z*. Double-focussing mass spectrometers also use an electrostatic sector to filter the secondary ions by kinetic energy either before or after the magnetic-sector. So-called 'sector-field' mass analysers allow high mass resolution to be achieved with high transmission, providing optimal conditions for high-precision elemental and isotopic analyses. The NanoSIMS 50 was designed for imaging with sub-micron lateral resolution. This is achieved by positioning the primary probe-forming lens parallel and very close to the sample, allowing the beam to be focused to a very small diameter. The primary ion beam impacts the sample surface at 90º, with the secondary ions extracted back through the same lens assembly. Two primary ion sources are available for the NanoSIMS: a Cs^+ thermal ionisation source for the generation of negative secondary ions (e.g., C, O, Si, halogens) which can be focussed to a sub-50 nm probe; and an O^- duoplasmatron source with a beam diameter of about 200 nm. In the last few years, a new RF plasma source has been developed producing a high-brightness O^- beam with a beam diameter of less than 100 nm. Images are acquired by rastering the primary ion beam over the sample (typically tens of micrometres), while electron multipliers are used to record the secondary ions at each pixel location. To use EM detectors count rates have to be kept low to avoid rapid ageing (less than 10^6 cps), which means that it is difficult to achieve the counting statistics necessary for high-precision isotope measurements. Nevertheless, elemental and isotopic images contain quantitative data, but matrix-matched standardisation is necessary to convert counts and ratios to 'real' values.

2. *ELEMENT AND ISOTOPIC MAPPING*

The high sensitivity and high spatial resolution of NanoSIMS allows the imaging of trace elements and isotopes within minerals at a level unachievable by any other technique. Elemental and isotopic maps of small grains can reveal complex chemical histories with changing environmental conditions (Fig. 1).

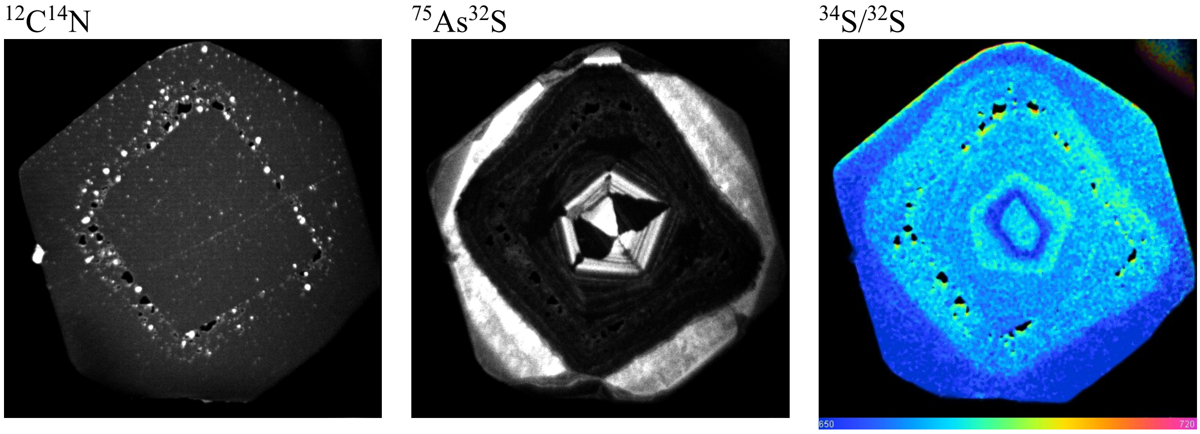

Figure 1. Elemental and isotope images of zoning in a sedimentary pyrite grain. The CN image reveals the presence of organic particles, suggesting the presence of S-metabolising microbes. The As image reveals changes in the composition of the mineralising environment, while the S isotope image indicates a change in the source of S. The field of view is 60 µm.

The high secondary ion yield of Au make SIMS is the ideal technique to analyse trace amounts of Au in sulphide minerals such as pyrite (FeS_2) and arsenopyrite (FeAsS). Other surface analytical techniques, such as EPMA, lack the sensitivity to detect very low concentrations of gold, even when the bulk-rock concentration is economically viable. This has led to the term 'Invisible Gold'. NanoSIMS, with its combination of high sensitivity and high lateral resolution has proved to be the ideal technique for mapping Au in Carlin-type deposits, where Au is present often only as micron-thick rims on sulphide minerals [2]. Furthermore, high sensitivity to other elements common in sulphide deposition, such as Te and Sb, mean that the intricate relationships between Au and associated elements can be investigated at the sub-micron scale revealing changes in the composition of the Au-bearing fluid over time [3]. To further constrain the evolution of the S-bearing fluid, relative changes in δ^{34}S can also be measured from regions with different trace element compositions. Most natural isotopic variations in terrestrial rocks are beyond the detection limits of the NanoSIMS, yet terrestrial fractionations in S isotopes can be relatively large; > 10s ‰. Barker *et al.* [2] demonstrated that the Au-rich rim of a single grain of pyrite exhibited a difference in δ^{34}S of 15 to 20 ‰ compared to the Au-poor core.

Isotope mapping can be particularly insightful when investigating the distribution of trace elements in zircon. Zircon is extensively used for geochronology due to its ability to incorporated U into its crystal structure. However, recently it has been shown that the distribution of radiogenic Pb within the matrix of very old zircons does not necessarily match that of the parent isotope, ^{238}U [4]. Fig. 2 shows NanoSIMS images of a 60x60 µm region of a zircon where the Pb is distributed in small sub-micron sized domains within a high Y and U bearing zone. This may have important implications for dating zircons as it assumes that the distribution of Pb matches the U.

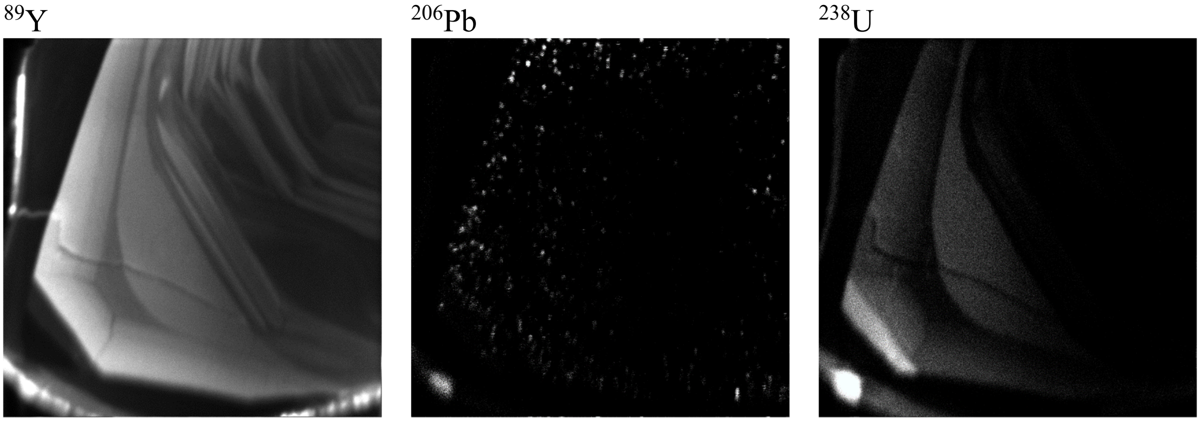

Figure 2. Elemental and isotope images of zoning in a zircon crystal. The ^{206}Pb shows a discreet punctate distribution unlike the ^{238}U. The field of view is 60 µm.

3. *ISOTOPE LABELLING*

In experimental petrology stable isotopes can be used to better understand the interactions between fluids and minerals. This technique is commonly used in biomedical and environmental experiments where the addition of an isotope label can be used to track to movement and uptake of particular elements and molecules by different components. Using stable isotopes, for examples ^{13}C in place of ^{12}C, is non-invasive as it does not significantly disturb the chemical composition of a system. As NanoSIMS can easily image isotopes of the same element simultaneously, it is a powerful tool for investigating the fate of a range of volatiles and fluids. Geisler *et al.* [5]

demonstrated this using ^{18}O-labelled water reacted with borosilicate glass beads to understand the mechanisms of glass erosion in an aqueous solution. This also works well for minerals, as shown by Spruzeniece *et al.* [6], who created complex symplectite textures by reacting feldspar samples in aqueous solutions.

4. CONCLUSIONS

Combining high sensitivity and high spatial resolution, NanoSIMS is a powerful tool for imaging very low concentration trace elements and isotopes in minerals. While not easily quantifiable, isotope imaging is useful to elucidate complex chemical interactions at the sub-micron scale.

5. ACKNOWLEDGEMENTS

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