CAMECA
SCIENCE & METROLOGY SOLUTIONS
/ AMETEK

NanoSIMS

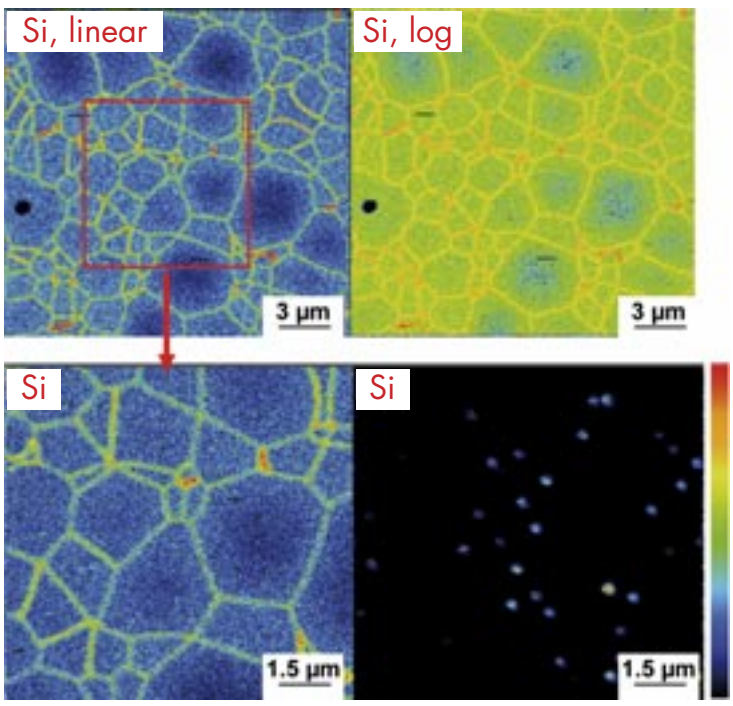
MATERIALS, GEOSCIENCES

Secondary Ion Mass Spectrometry for Imaging & Measurement of Trace Elements & Isotopes at High Resolution

50nm spatial resolution for sharp chemical or isotopic imaging

Trace level elemental sensitivity from deep sub-micron areas

Parallel collection of up to 7 species for simultaneous isotopic and/or elemental analysis



Top row:
Silicon dopant mapping (linear and log. display) in YAG samples (Ytrium Aluminium Garnet).

Bottom row:
Silicon dopant mapping at higher magnification on two different YAG, showing two different segregation patterns after thermal treatment.

Courtesy of Dr. H. Haneda,
National Institute for Materials Science,
Tsukuba, Ibaraki, Japan.

NanoSIMS 50L

Introduction to the SIMS technique

Secondary Ion Mass Spectrometry (SIMS) is based upon the sputtering of a few atomic layers from the surface of a sample, induced by a "primary ion" bombardment. Molecules are broken, atoms and atomic clusters are ejected, some of them being spontaneously ionized. These "secondary ions" are a characteristic of the composition of the analyzed area. They are separated according to their mass, and an image containing quantitative information is formed for a selected mass.

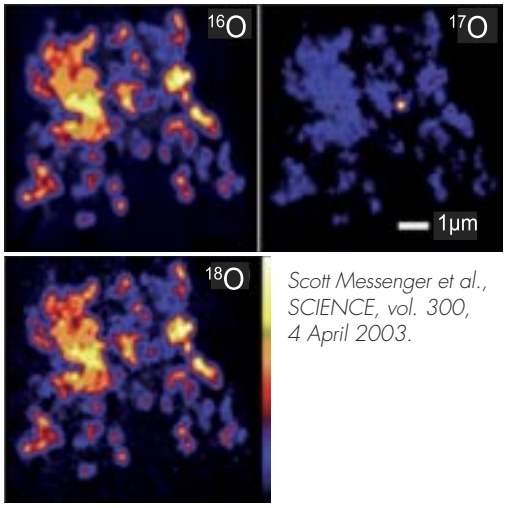
The **NanoSIMS** is a totally unique analytical instrument offering **high spatial resolution** (50nm) together with **ultra-high sensitivity** for localized isotope ratio or trace element analysis.

Precise isotopic measurement from small volumes

Cosmochemistry

Individual isotopic analysis of Interstellar Dust Particles and **sub-micron grains** in meteorites is now possible with the **NanoSIMS** microprobe. The small volume of matter available (0.1-0.3µm in size) limits the statistics through the minor isotope intensity. The rare, precious grains must be fully sputtered with optimized conditions: a few pA of reactive primary ions, maximum transmission at high mass resolution, parallel detection.

Samples of stars beyond the solar system: Silicate Grains in Interplanetary Dust. Oxygen isotopic images of a slice of IDP 0005 C13. A 0.25µm presolar grain with a large ^{17}O excess can be clearly seen in the ^{17}O image, signing its extra solar system origin.



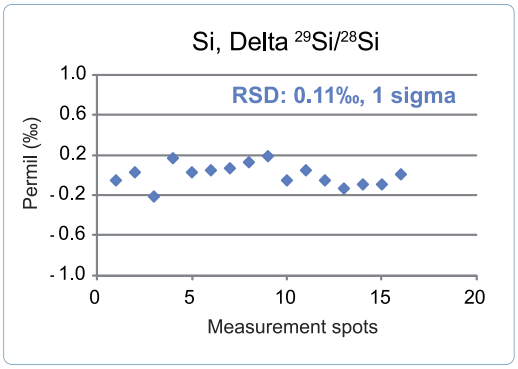
Scott Messenger et al., SCIENCE, vol. 300, 4 April 2003.

Earth sciences

The isotopic ratio reproducibility obtained on the **NanoSIMS** with **Electron Multipliers** is typically at **permil level** (provided the statistics is sufficient). Applications requiring a better level of precision and reproducibility are done with **multiple Faraday Cups** (each detector can be equipped with both EM and FC) and higher primary current. The new primary ion column can deliver up to 10-20nA with spot size of a few microns.

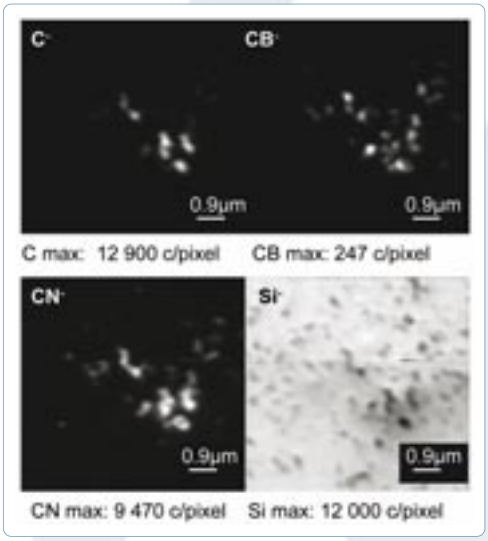
Sub-permil reproducibility is then obtained in automated mode due to an exceptional design and automated alignment routines. The parallel collection ensures that the different detector signals come from the exact same micro-volume.

Silicon sample analyzed in FC/FC mode
$^{29}Si/^{28}Si$: RSD 0.11 ‰ 1 sigma.
$^{30}Si/^{28}Si$: RSD = 0.17 ‰ 1 sigma
16 craters of 12x12µm over 8x8mm.
Ip: 1.9nA, Spot size: 1.5µm, MRP: 7000



High sensitivity together with high lateral resolution

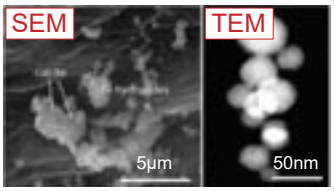
Fragile and insulating materials



"Dark spots" in bulk Si_3N_4 (1mm thick sample). A typical case where the small size of the spots makes the analysis difficult with other conventional techniques: TEM/EDS-ELS requires tedious and not always feasible sample thinning and has limited sensitivity, particularly for light elements; Auger is unusable here due to the charging problem.

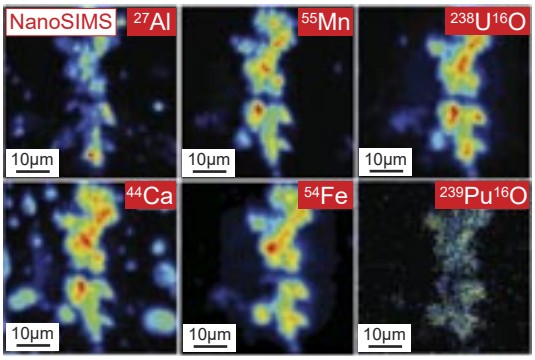
Note the **sensitivity of the NanoSIMS**: at high mass resolution, the signal of carbon, silicon or nitrogen is around 10,000 counts per single pixel indicating detection limits on C, N or Si in the 100 ppm range together with a 100nm lateral resolution. Summing pixel signal inside small ROIs (regions of interest) allows to reach ppm detection limit from deep sub-µm areas.

Field: 6x6µm. 16 keV Cs+ beam 100nm/1.5 pA. Acquisition time: 22min.
Courtesy of G. Barbier, Céramétal, Luxembourg.



Nuclear contamination study

Colloids were identified as a possible source of long-distance transport of plutonium in the groundwater from the Mayak Production Association, Urals, Russia.

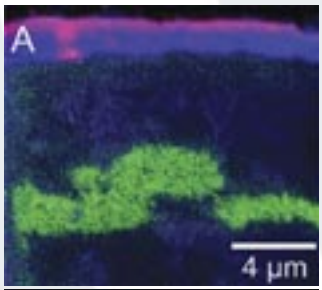


SEM-EDS is used to detect major elements. TEM permits nm-level structure analysis. Thanks to its **unique imaging sensitivity**, the NanoSIMS delivers elemental maps which reveal that amorphous iron oxide colloids adsorb Pu(IV) hydroxides or carbonates along with uranium carbonates.

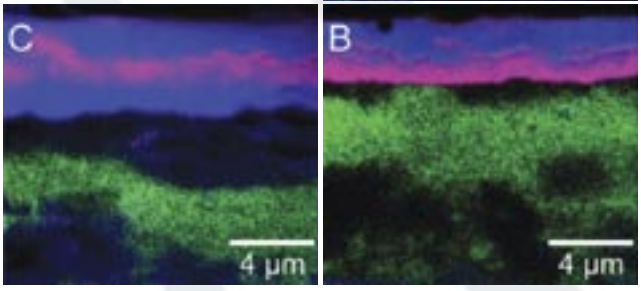
A. P. Novikov et al., SCIENCE, vol. 314, 27 October 2006.

Oxidation study using isotopic tracers

The complex multi-step oxidation mechanism of zirconium alloy under pressurized hot water was elucidated by imaging, in the cross-section, the incorporation of stable isotope tracers (D and ^{18}O) in the surface oxide(s) and/or in the metal. The oxide grown after 34 days oxidation is protective; the one obtained after 80 days becomes porous with defects and a new layer of metal is oxidized below it; the one obtained after 160 days is protective again. Hydrides are formed below the surface.



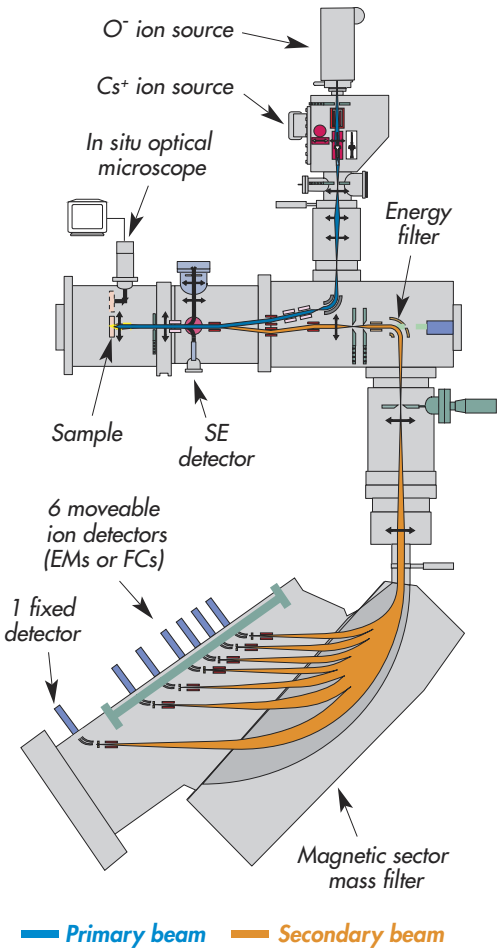
RGB colour merge image of
^{18}O (red), **^{16}O (blue)** and **^{2}H (green)**.
Low tin ZIRLO™ samples **spiked 20 days with ^{18}O- and ^{2}H-labeled pressurized water** after:
(A) 34-day oxidation in pressurized water,
(B) 80-day oxidation,
(C) 160-day oxidation.



Courtesy of S. Yardley et al., J. Nucl. Mater. 443 (2013) 436–443.

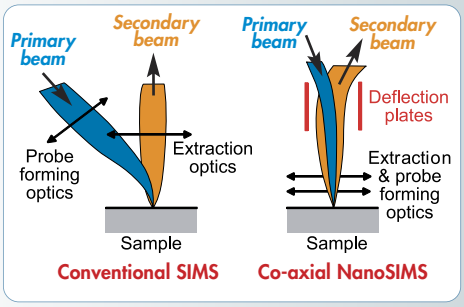
NanoSIMS:
An advanced design

Synopsis of a CAMECA NanoSIMS 50L

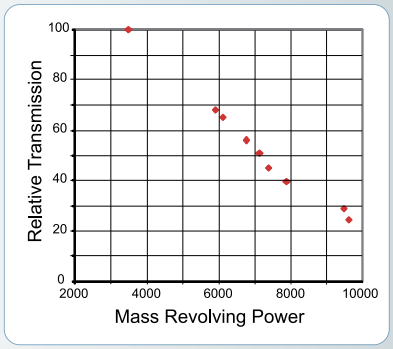


The **NanoSIMS** is based on an original design by Pr. Slodzian, University of Paris Sud, France. Cs^+ or O^- primary ions are focused and rastered on the surface of the sample, at normal incidence. The ions sputtered by this primary beam are collected, and the secondary ion beam is shaped in order to be mass analyzed. Seven detectors are available at the exit of the mass analyzer, six of them being moveable. Up to seven ionic species can be simultaneously recorded, originating from the exact same sputtered volume, ensuring reliable isotopic or elemental ratio and perfect distribution comparison.

The short working distance of the probe forming lens/extraction ensures:
***1)** smaller spot size for a given beam current*
***2)** higher collection efficiency*
Co-axial geometry also minimizes shadowing and topography effects.



The double focusing Mattauch-Herzog-like geometry and optimized transfer optics guarantee high transmission at high mass resolution, required for analysis of small volumes of complex materials. Compared to pulsed/alternated TOF-SIMS instruments, the NanoSIMS DC operational mode ensures a sensitivity higher by several orders of magnitude, and the mass resolution is independent from the spot size choice.



All options are field-retrofittable (charge compensation, SEM detector, multiple FCs, …).

CAMECA is the world premier provider of microanalytical instrumentation. We deliver cutting-edge science and metrology solutions, and offer our customers unparalleled support and maintenance service through the comprehensive AMECARE program.

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