Innovative Detection Strategies on Large-Geometry SIMS

Complementary EM & FC approach

Secondary Ion Mass Spectrometry (SIMS) using the large-geometry, multi-collector CAMECA ion microprobe is particularly well suited for in-situ, high precision isotope ratio measurements at high lateral resolution (tens of µm down to sub-µm range).

For some challenging applications such as $^{36}S/^{32}S$ isotope ratio in sulfides, $^{17}O/^{16}O$ isotope ratio in oxides or other studies requiring the measurement of low abundance isotopes at fine scale, measurement of low signal intensities is required. Traditionally, count rates between the upper level of pulse counting systems ~10^5 c/s and the lower level of Faraday Cup (FC) measurements ~10^6 c/s are considered to be in a "gap area" where neither detection protocol can achieve performance better than the 1‰ level.

FC detectors offer high precision with no need for gain monitoring, however the uncertainty of FC measurements depends on the signal to noise ratio. One approach for measuring low signal intensities is to use FCs coupled to electrometers with high ohmic resistors, as the noise is expected to decrease with the inverse square root of the resistor value. The IMS 1300-HR³ can now be equipped with low noise 10^{12} Ω resistor FC preamplifier boards for measuring signal intensities down to the ~3 x 10^5 c/s range with precision better than the 0.5‰ level (1SD), see Figures 1 and 3.

A complementary approach consists of using discrete-dynode pulse counting electron multiplier (EM) detectors, provided that EM gain drift and aging effects are minimized. In the CAMECA acquisition software module, a fast iterative algorithm adjusts the EM high voltage before each isotopic ratio measurement in order to keep a constant EM gain through the whole dataset. Results shown in Figure 2 demonstrate that 0.3‰ isotopic reproducibility (1SD) is achievable in automated mode, working with EM detectors and count rates up to 5x10^5 c/s.

Recent innovation on LG-SIMS detectors allows filling the gap between the EM and FC detection range, see Figure 3. Challenging applications such as quadruple sulfur or triple oxygen isotope measurements can now be addressed with no compromise on lateral resolution and data precision.

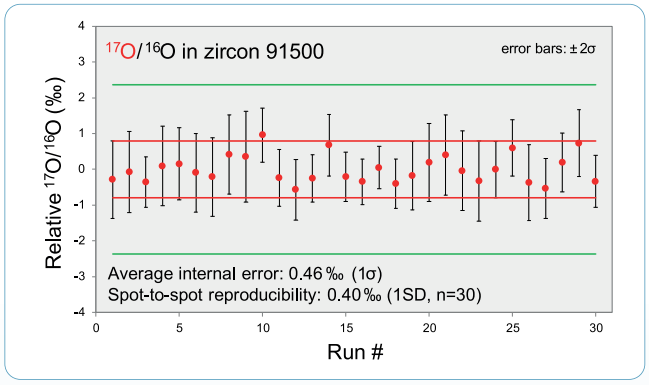


Fig. 1: Excellent $^{17}O/^{16}O$ precision, ^{17}O signal ~ 3.4x10^5 c/s on FC 10^{12} Ω.
$^{17}O/^{16}O$ isotope ratio in zircon 91500, multicollection 3-isotopes FC/FC/FC mode, mass resolution ~7 000 on ^{17}O. FC offset monitoring for every measurement during pre-sputtering, fully automated analysis session. 20 cycles x 4 sec integration time, ~4 min/spot; The red lines show the expected dispersion (-2σ,+ 2σ) for FC 10^{12} Ω whereas the green lines show the expected dispersion (-2σ,+ 2σ) if a FC 10^{11} Ω had been used for ^{17}O detection.

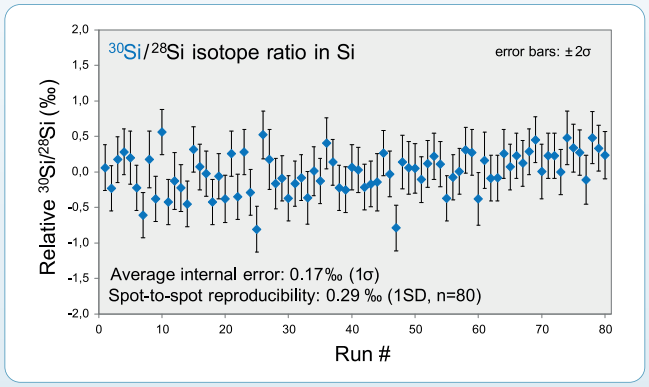


Fig. 2: Excellent $^{30}Si/^{28}Si$ precision, ^{30}Si signal ~ 5x10^5 c/s on multicollection EM
$^{30}Si/^{28}Si$ isotope ratio in Si, multicollection FC/EM mode, mass resolution ~2 500. EM high voltage automatically adjusted before each measurement to minimize EM drift, fully automated analysis session. 20 cycles x 4 sec integration time, ~4 min/spot. The EM voltage varied ~15 V during the analysis session; if not corrected, the isotope ratio would have drifted by ~3.7‰.

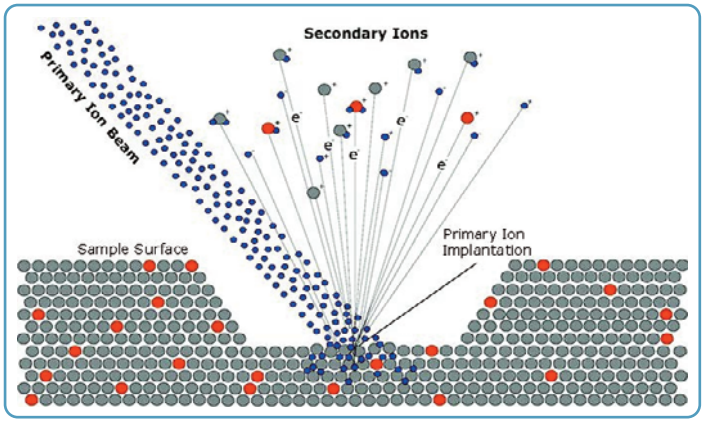
Isotope ratio	^{17}O count rate (c/s)	Total int. time (sec.)	Expected uncertainty (‰) FC 10^{12} Ω	EM
$^{17}O/^{16}O$	1.0x10^5	80	1.34	0.35
$^{17}O/^{16}O$	2.0x10^5	80	0.67	0.25
$^{17}O/^{16}O$	3.5x10^5	80	0.38	0.19
$^{17}O/^{16}O$	5.0x10^5	80	0.27	0.16
$^{17}O/^{16}O$	7.5x10^5	80	0.18	0.13
$^{17}O/^{16}O$	1.0x10^6	80	0.13	0.11

EM

FC 10^{12} Ω

Fig. 3: No EM-FC detection gap thanks to EM HV adjust routine and low noise FC 10^{12} Ω detector.
The FC 10^{12} Ω detector expected uncertainty is better than 0.5 ‰ for signals down to ~3 x 10^5 c/s, whereas the EM detector is appropriate for signal intensities up to ~5 x 10^5 c/s using the automated EM HV adjust control to minimize EM drift (see Fig. 2).

The Technique Behind



Dynamic SIMS

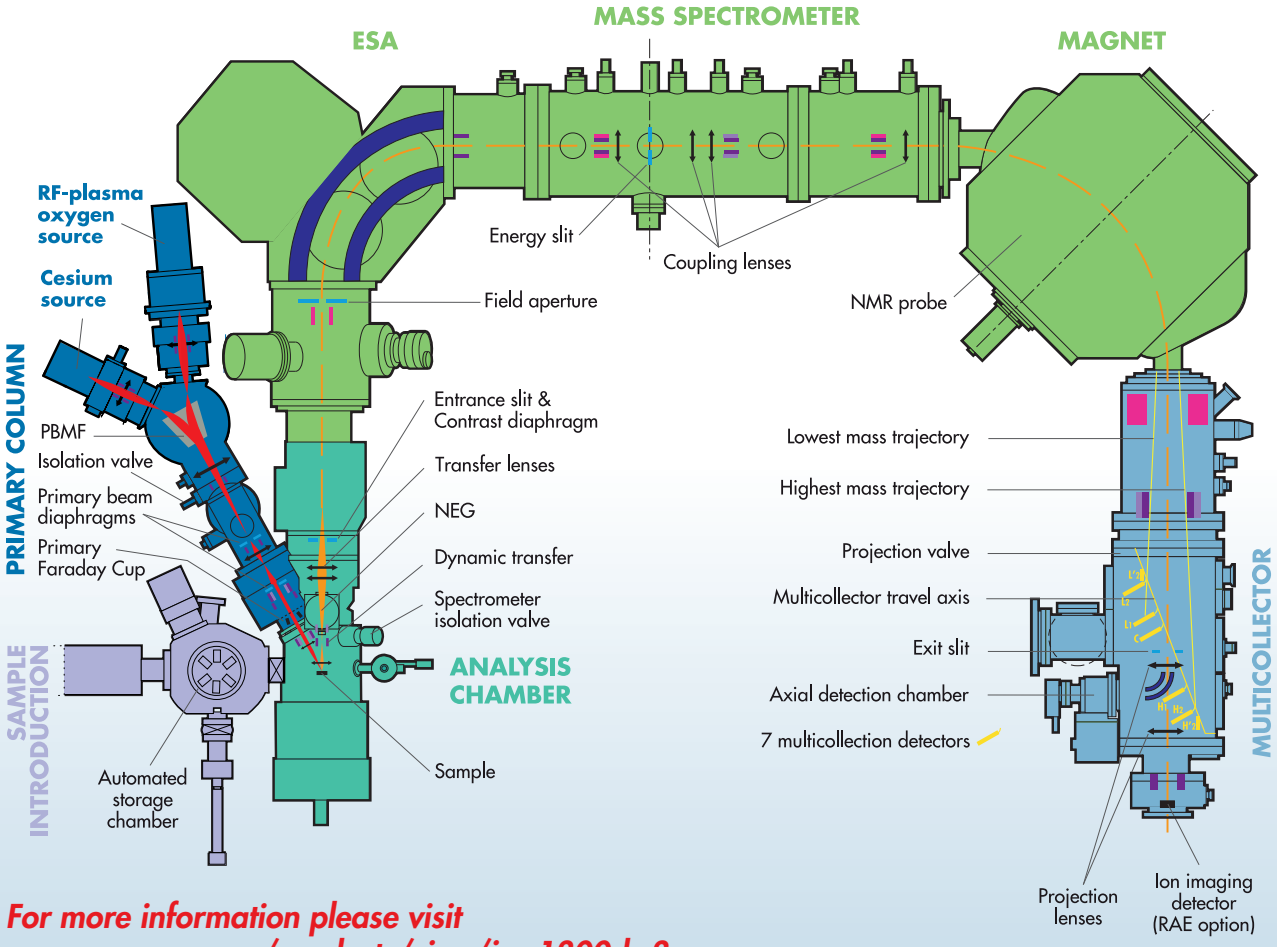
When a solid sample is sputtered by primary ions of few keV energy, a fraction of the particles emitted from the target is ionized. Secondary Ion Mass Spectrometry consists of analyzing these secondary ions with a mass spectrometer.

The SIMS technique is "destructive" by its nature (sputtering of material). It can be applied to any type of flat, solid material that can be kept under vacuum.

In dynamic SIMS, bulk composition and in-depth distribution of trace elements are investigated with a depth resolution ranging from sub-nm to tens of nm. SIMS is recognized as the most sensitive elemental and isotopic surface analysis technique.

CAMECA IMS 1300-HR³

The latest generation multicollection Large-Geometry SIMS is equipped with a high-brightness RF-plasma oxygen ion source in addition to the cesium microbeam source. It also includes an automated storage chamber for analysis of multiple mounts in chained mode.



For more information please visit
www.cameca.com/products/sims/ims1300-hr3

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