Innovative Detection Strategies on Large Geometry SIMS open new challenging applications for light isotope ratio analyses

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Large Geometry Secondary Ion Mass Spectrometry (LG-SIMS), operating in multicollection mode, allows high precision light isotope ratio measurements at high lateral resolution (tens of μm down to sub-μm range). For some challenging applications involving fine scale analysis of low abundance isotopes (i.e. $^{17}$O or $^{36}$S) or low-concentration elements (i.e. nitrogen in diamonds) 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.

Faraday Cup detectors (FC) 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. CAMECA LG-SIMS can now be equipped with low noise $10^{12} \Omega$ resistor FC preamplifier boards for measuring signal intensities down to the ~$3 \times 10^5$ c/s range with precision better than the 0.5‰ level (1SD).

For measurement of low-abundance isotopes, a complementary approach consists of using discrete-dynode pulse counting electron multiplier (EM) detectors, for which drift and aging effects are minimized using a fast automated EM high voltage adjustment routine.

During this PICO presentation, we will discuss the relevance of the detector choice (FC $10^{12} \Omega$ vs EM) for few examples of innovative applications.

Example of mass independent fractionation:

In addition to classical isotopic ratio measurements (e.g. $\delta^{13}$C, $\delta^{15}$N, $\delta^{18}$O or $\delta^{34}$S), for which the instrumental mass fractionation (IMF) correction is mostly limited by the natural heterogeneity (chemical and isotopic) of the reference material, SIMS is particularly well suited for the measurement of mass independent fractionation (MIF, e.g. $\Delta^{33}$S, $\Delta^{36}$S and $\Delta^{17}$O). Along with classical geochemical processes, the degree of isotopic fractionation scales with the difference in mass of the isotopes involved (i.e. $\delta^{32}$S = 0.515 * $\delta^{34}$S). MIF refers to non-conventional ratios that depart from these mass dependent rules. As instrumental mass fractionation has been shown to
be strictly mass dependent, MIF measurements are not subject to IMF correction and are therefore measured directly. The use of SIMS in this specific case is particularly well suited and allows to fully explore the rich phenomenology of MIF source processes. We will discuss the advantages and disadvantages of using FC $10^{12}$ Ω for the minor Sulphur isotope ($^{36}$S) measurement.

Carbon and Nitrogen in diamond:

We will also show a recent analytical development aiming to measure δ$^{13}$C in diamonds at mass resolution of ~5000 (allowing the full separation of $^{13}$C- and $^{12}$CH-) as well as N-content and N-isotopes in diamonds at a mass resolution of ~9000 (full separation of $^{12}$C$^{14}$N- and $^{13}$C$^{13}$C-). For this purpose, the use of FC $10^{12}$ Ω greatly improves the data quality and allows the simultaneous measurement of N-content and δ$^{15}$N.