CAMECA IMS 7f-GEO: Specialized SIMS tool for geosciences

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ABSTRACT

SIMS is applied to a wide variety of applications in geosciences, as it offers both sensitivity and *in situ* isotopic and/or elemental analysis of solid samples. CAMECA has introduced the IMS 7f-GEO, a compact SIMS model designed to meet the high precision/high throughput requirements of stable isotope and trace element analysis. For high precision/high throughput measurements, the detectors choice is the first issue to consider. It is well known that Faraday Cups (FCs) are preferred to Electron Multipliers (EMs) provided the secondary ion intensities are high enough. Secondly, in the absence of parallel detection, it is crucial to perform the switching between the different species as fast as possible, and to monitor all relevant parameters that may compromise the achievable precision. The IMS 7f-GEO has been designed to meet these instrumental performance requirements.

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1. Introduction

The success of the SIMS technique in the geosciences field relies on its performance in terms of: (1) great sensitivity which is mandatory for high precision measurements or to achieve low detection limits; (2) elemental as well as isotopic information ranging from low mass (H) to high mass (U) species; (3) in situ analysis of any solid flat polished surface; (4) high spatial resolution from tens of microns down to sub-micron scale.

Different types of SIMS instruments have been developed in order to meet the high performance requirements of the cosmo- and geochemistry research fields.

CAMECA IMS 1280 large SIMS instrument offers outstanding performance for the entire application range, as it provides the highest transmission at high mass resolution [1,2] and a versatile multicollection system. CAMECA NanoSIMS is also a large multi-collection SIMS instrument which has been designed in order to attain optimized spatial resolution (down to 50 nm for Cs primary beam) in daily basis use [3].

The newly developed IMS 7f-GEO is a mono-collection compact SIMS model which is well suited for high precision stable isotope and trace element analysis. This tool is particularly targeted to laboratories working on these applications mainly, for which the IMS 1280 and NanoSIMS could be seen as oversized.

In order to achieve both high precision and high throughput, the detectors choice is the first issue to consider. It is well known that Faraday Cups (FCs) are preferred to Electron Multipliers (EMs)

provided the secondary ion intensities are high enough. Secondly, in the absence of parallel detection, it is crucial to perform the switching between the different species as fast as possible, and to monitor all relevant parameters that may compromise the achievable precision.

The IMS 7f-GEO has been designed to meet these instrumental performance requirements.

Detailed instrumental features and experimental data are presented in the next sections.

2. Experimental

2.1. Instrumental features

The key features of this new instrument are:

(a) Quasi-continuous primary intensity record:

An accurate primary intensity (Ip) measurement is obtained from the combination of a primary Faraday Cup equipped with a repeller and working in charge mode, and a fast beam blanking. For every elementary acquisition (80 ms), a given percentage (computer controlled) is dedicated to the Ip measurement. Therefore, one Ip value is returned per data point. This allows a more reliable primary beam drift correction, therefore minimizing short-term instrumental stability effects.

(b) Magnetic sector with fast peak switching capability:

It consists of a combination of magnetic and electrostatic beam deflection. For a mass jump from M1 to M2, the settling time for the magnetic field to vary from B1 to B2 is determined

Table 1
Switching time values (s) for different mass jumps and MRP values, using the magnetic sector with the fast switching capability

MRP (flat top peak)	400	2000	3000	5000
Mass jump	Switching time (s)			
16–18, 18–16	0.08	0.24	0.32	0.40
28–29, 29–30	0.08	0.16	0.16	0.16
28–30, 30–28	0.08	0.16	0.24	0.24
30–56	0.24	n.a.	n.a.	0.72
56–30	0.64	n.a.	n.a.	1.04
28–181	0.88	n.a.	n.a.	1.52
181–28	1.04	n.a.	n.a.	1.76

by three different physical processes: the available voltage V at the magnet coil terminals, the time constant of the magnet control system and the eddy currents arising in conductor pieces. During a mass jump, the Hall probe measures in real time the $B(t)$ field variation from B_1 to B_2. This Hall probe signal can then be used to apply the electrostatic voltage $V(t)$ feedback on the magnet flight tube in order to compensate for the B field gap $\Delta B(t) = B_2 - B(t)$. This voltage rapidly deflects the secondary beam, which allows to speed up the peak positioning in the exit slit plane. Compared to a pure Electrostatic Peak Switching (EPS) [4], working at fixed B field and providing extremely fast commutation time (0.1 s), this new system has the advantage of being applicable over the full mass range, the waiting time values being as short as 0.3 s for high mass resolution analyses (Table 1). It provides benefits in terms of precision and analysis throughput. Note that a pure EPS mode is also available on the IMS 7f-GEO.

(c) Sextupole at the entrance of the magnet:

This device, placed near the entrance of the magnet, allows to cancel second-order geometrical aberrations. It is then possible to use a larger field aperture for the same mass resolution power (MRP). It provides higher instrument transmission at high MRP (Fig. 1).

(d) Double Faraday Cup system:

The detection system of the IMS 7f consists of an Electron Multiplier and a pair of Faraday Cups localized on both sides of
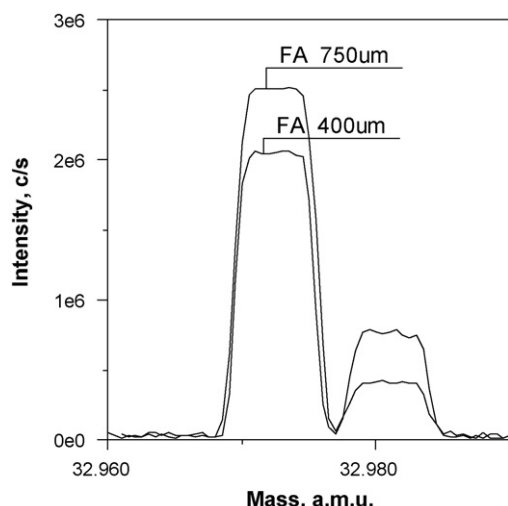
the EM. The detector selection is made by means of an electrostatic deflection. A fast secondary beam blanking system allows to control exactly the time the secondary beam is addressed into each FC channel. Each detector can accommodate two different resistors (e.g. 10^{10} Ω for ^{16}O and 10^{11} Ω for ^{18}O measurement). The charges collected by the FCs are measured with two independent acquisition channels. These FCs can therefore be run in charge mode with no need for FC settling time between the two isotopes, thus shortening the total acquisition time. This configuration makes possible to run analyses in a pseudo-bicollection mode well suited for stable isotope high precision analysis.

(e) High precision Faraday Cup electrometers:

The FCs electrometer amplifier system is developed by CAMECA. It minimizes the short-term detector noise and guarantees a long-term stable baseline. The noise (1σ) is lower than 4×10^{-16} A for 4 s integration time, and the baseline drift is lower than 4×10^{-16} A over 1 h for 64 s integration time.

(f) FCe channel:

In the case of insulating materials under Cs^+ primary beam bombardment, the charging effect is compensated by means of an electron beam. Perfect charge neutralization over the sputtered area is a critical parameter for achieving routinely sub-per mil precision. A Faraday Cup (FCe) dedicated to the current measurement of the reflected electron beam by the sample surface was implemented in the IMS7f-GEO. Special software tools, integrated in the acquisition module, use the FCe current measurement in order to center the electron beam flooding on the sample before each analysis.

2.2. Expected analytical performance

The typical IMS 7f-GEO analytical performance for stable isotope analysis using FC/FC charge mode is exemplified in Table 2 for the $^{18}O/^{16}O$ ratio. For a 2×10^6 c/s intensity, and 40 s total integration time for ^{18}O, a precision better than 0.5 per mil is expected. The total acquisition time (including waiting times and ^{16}O integration time) is 56 s.

Instead, in the EM/EM mode, the ^{18}O intensity is limited to 2×10^3 c/s, since the ^{16}O intensity is at maximum 1×10^6 c/s. According to the Poisson statistics, an error of 0.5 per mil requires a total acquisition time of 2000 s for the minor isotope. This corresponds to a total acquisition time of ~3000 s, waiting times and integration time for the major isotope included.

3. Results and discussions

3.1. Oxygen isotope analysis

The analyses were performed using Cs^+ primary ions with 20 keV impact energy. A probe of ~5 μm carrying 3 nA was rastered over an area of 10 $\mu m \times 10$ μm. The analyses were performed using a mass resolution of 2500, in order to resolve the $^{18}O/^{16}O^1H_2$ interference.

Fig. 1. Mass spectra obtained with two different field apertures (FA): 750 and 400 μm. The larger FA gives a higher transmission: increase of the ^{33}S signal of 22% (left peak), while keeping a flat top peak. The mass resolution power (MRP) is 4300 (10%) for FA 750 μm, and 4500 (10%) for FA 400 μm. Signal on the right corresponds to $^{32}S^1H$ interference; its intensity is related with the surface contamination conditions only.

Table 2
Typical total acquisition time (s) allowing to reach a precision of 0.5 per mil, for an analysis performed using the EM/EM mode, and an analysis performed using FC/FC charge mode

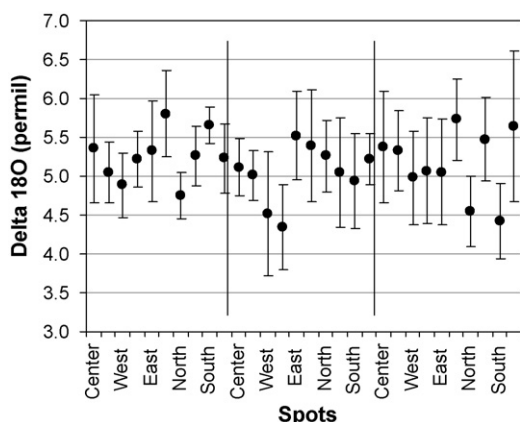| Mode	Total acquisition time (s)
EM/EM	~3000
FC/FC (charge mode)	56

Fig. 2. Measured oxygen isotopic ratio, each data point corresponding to a different spot of the sample. The runs were distributed over an area of 15 mm in Ø across the sample. Errors bars correspond to ±2σ.

Table 3
REE ratio measurements, comparison between experimental standard error mean and Poisson statistics

Ratio	Mean	S.E. %	Poisson %
139La/28Si	7.15E−04	0.14	0.11
140Ce/28Si	6.18E−04	0.12	0.12
141Pr/28Si	7.45E−04	0.13	0.11
143Nd/28Si	9.12E−05	0.12	0.22
149Sm/28Si	1.14E−04	0.15	0.20
151Eu/28Si	3.97E−04	0.12	0.15
157Gd/28Si	2.42E−04	0.24	0.14
159Tb/28Si	6.96E−04	0.07	0.12
161Dy/28Si	1.35E−04	0.21	0.18
165Ho/28Si	6.68E−04	0.14	0.12
167Er/28Si	1.65E−04	0.11	0.17
169Tm/28Si	6.31E−04	0.15	0.12
172Yb/28Si	1.49E−04	0.22	0.18
175Lu/28Si	5.54E−04	0.13	0.13

The electron gun was used for charge compensation. An automatic electron beam centering was performed before each analysis.

A standard deviation of 0.37 per mil and a mean internal error of 0.27 per mil were achieved (Fig. 2).

The delta ^{18}O (SMOW) values presented in Fig. 2 are not corrected for the instrumental mass fractionation. An average measured value of 5.1 ± 0.4 per mil was obtained over all data points. The nominal delta ^{18}O (SMOW) for this sample is 12.3×0.4 per mil (value obtained on the IMS 1280 using NBS28 sample as standard). Therefore, the instrumental mass fractionation on the IMS 7f-GEO is around −3.5 per mil/amu.

Ratio values given in this section and the following are corrected for the relative yield of the two FC detectors. The precision of this yield measurement, performed by applying the same reference voltage signal on each detector, is better than 0.1 per mil.

3.2. Silicon isotope analysis

The analyses were performed using O$^-$ primary ions with 23 keV impact energy. A static projected primary current of 4 nA was used. The analyses were performed using a mass resolution of 2500, in order to resolve the ^{30}Si/^{28}O^{1}H$_2$ interference. A quartz synthetic sample was used.

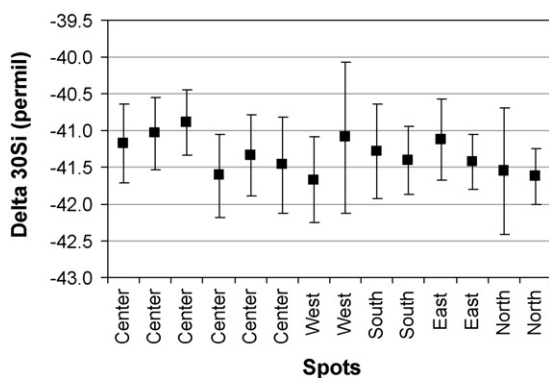A standard deviation of 0.25 per mil and a mean internal error of 0.29 per mil were achieved (Fig. 3).

Fig. 3. Measured silicon isotopic ratio, each data point corresponding to a different spot of the sample. The runs were distributed over an area of 15 mm in Ø across the sample. Errors bars correspond to ±2σ.

No mass fractionation correction has been applied to delta ^{30}Si values presented in Fig. 3 (normalized to ^{30}Si/^{28}Si reference ratio of 0.0336214). The mass fractionation cannot be computed as the nominal delta ^{30}Si value is unknown for this sample. Results obtained on two different IMS 7f-GEO differ by less than 2 per mil demonstrating a stable mass fractionation from tool to tool.

3.3. Sulfur isotope analysis

Analyses were performed on Balmat pyrite standard sample using Cs$^+$ primary ions with 20 keV impact energy. A primary beam of 0.4 nA was rastered over 10 μm. The analyses were performed using a mass resolution of 4000, in order to resolve the ^{34}S/^{32}S^{1}H$_2$ interference.

A standard deviation of 0.20 per mil and a mean internal error of 0.23 per mil were achieved over a series of eight different spots.

The QSA effect [5] is known to affect the intensities measured on EM detectors, for isotopes presenting an important concentration level in the sample and a high ionization yield. Note that the Faraday Cup collection system of the IMS 7f-GEO allows to overcome this effect.

3.4. REE analysis

Analyses were performed using O$_2$$^-$ primary ions with 23 keV impact energy, a static projected primary current of 7 nA, and by applying the energy filtering technique. The NBS610 synthetic standard sample from NIST was used. The experimental errors are in the sub-percent level, and are determined by statistics (Table 3).

4. Conclusions

CAMECA recently introduced the IMS 7f-GEO, a compact SIMS model specially dedicated to stable isotope and trace element analysis. The key instrumental features of this instrument, including Faraday Cups detection and fast peak switching capabilities, are detailed. The experimental data obtained on this instrument demonstrate that a precision in the sub-per mil range can be achieved on daily basis use for different stable isotopic ratio analyses on oxygen, silicon, sulfur.

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