Application Note: 30001

High Precision Measurement of Magnesium to Calcium and Strontium to Calcium Elemental Ratios

Key Words

- ELEMENT 2
- Elemental Ratios
- High Resolution ICP-MS

Summary

A simple and rapid procedure for routine high precision measurement of Sr/Ca and Mg/Ca elemental ratios is presented. The Thermo Scientific ELEMENT 2, a single collector double focusing ICP-MS, was used to measure Sr/Ca and Mg/Ca elemental ratios in microgram samples of corals. The concentrations of Sr, Mg and Ca were determined using external calibration with ^{103}Rh as internal standard. The calibration curves had correlation coefficients > 0.99996 (Figure 1). The external precision of Sr/Ca and Mg/Ca was 0.07% RSD. The analysis time for the determination of both ratios in a single sample (5 replicate analyses) was 12 minutes.

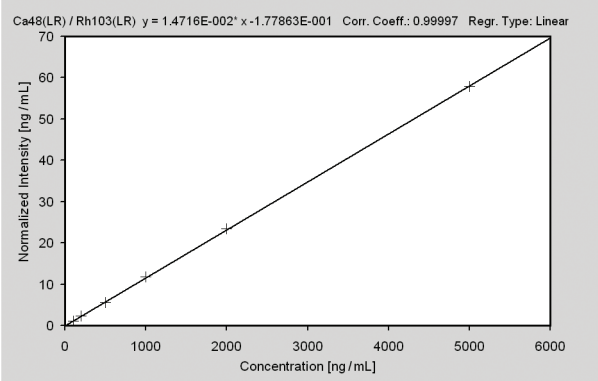

Figure 1: Thermo Scientific ELEMENT 2 HR-ICP-MS calibration curve for Ca.

Introduction

Because the Sr and Mg contents of corals are sensitive to the water temperature at the time of deposition, the Sr/Ca and Mg/Ca ratios in fossil corals can be used as proxy indicators of past surface water temperatures. Because the temperature dependence is small, high precision analyses are required. Thermal ionization mass spectrometry (TIMS) has been the preferred method because of its excellent precision (< 0.02% RSD). However, there has been considerable interest in investigating other techniques to provide higher sample throughput while maintaining the high precision, e.g. ICP-QMS[1-3], ICP-OES[4], LA-ICP-QMS[5], ion probe[6] and HR-ICP-MS[7,8]. The major analytical challenge is to achieve very high precision elemental ratios for elements at widely different concentrations (Ca:Sr:Mg = 1000:20:3). In this report, we present a simple and rapid procedure for routine high precision measurement of Sr/Ca and Mg/Ca elemental ratios (< 0.1% RSD) with the ELEMENT 2.

Experimental

Coral samples (100 mg) were dissolved in 2% nitric acid (100 mL) and spiked with ^{103}Rh as internal standard (200 ng/mL). The samples were then diluted 1000 fold before analysis. Calibration standards used were in the range 100 – 5000 ng/mL Ca, 2 – 100 ng/mL Sr, and 0.5 – 10 ng/mL Mg (Figure 1 and 3). The external precision of the Sr/Ca and Mg/Ca elemental ratios were calculated from 5 determinations of the concentration ratios in the sample.

The analysis procedure used, including blank, concentration standards and samples is shown in Figure 2. The outline of the autosampler system used (CETAC ASX-100) is also displayed. The experimental parameters are summarized in Table 1.

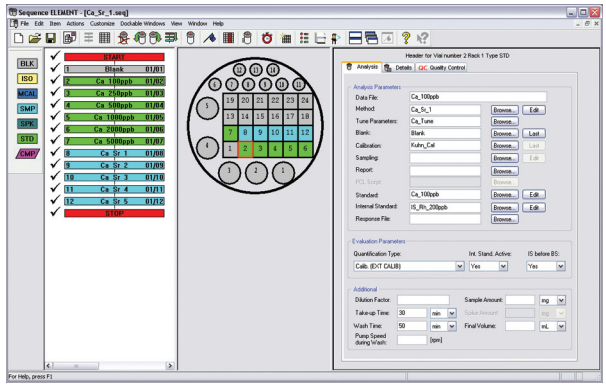

Figure 2 Screen capture from the Sequence Editor of the Thermo Scientific ELEMENT 2 software, showing the Sequence used for the measurement of Sr/Ca and Mg/Ca elemental ratios.

Forward power:	1238 W
Reflected power:	< 2 W
Coolant gas flow:	16 L/min
Auxiliary gas flow:	0.82 L/min
Sample gas flow:	0.78 L/min
Sample introduction:	Stable Sample Introduction System: - PFA nebulizer (60 µL/min uptake rate) - dual spray chamber

Table 1: Experimental ICP-MS parameters.

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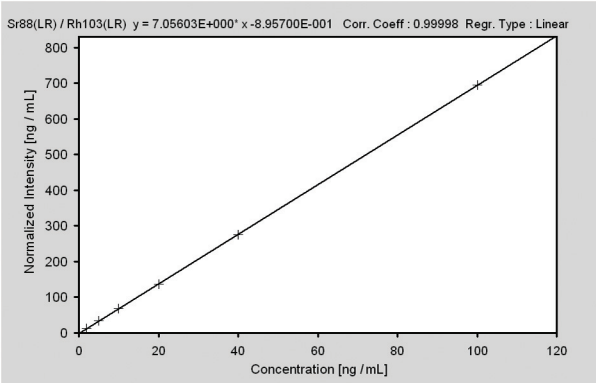

Figure 3: Thermo Scientific ELEMENT 2 HR-ICP-MS calibration curve for Sr.

Results and Discussion

The calibration curves for the determination of Ca and Sr concentrations in the coral sample are shown in Figures 1 and 3.

The precision for each calibration point was < 1% RSD throughout the analysis sequence.

The correlation coefficients for all calibration curves were > 0.99996 (Figure 3).

The results of the Sr/Ca and Mg/Ca elemental ratio calculations are summarized in Tables 2 and 3.

ISOTOPE	CONCENTRATION [NG/ML]				
	RUN1	RUN 2	RUN 3	RUN 4	RUN 5
^{48}Ca (Low Resolution)	1665.2	1652.2	1647.3	1643.2	1640.5
^{88}Sr (Low Resolution)	32.64	32.34	32.28	32.21	32.17
Sr/Ca0.019601	0.019576	0.019594	0.019602	0.019612	

RATIO	AVER	STD. DEV.	RSD[%]
Sr/Ca	0.019597	0.0000134	0.07

Table 2: Sr/Ca elemental ratio calculations.

ISOTOPE	CONCENTRATION [NG/ML]				
	RUN1	RUN 2	RUN 3	RUN 4	RUN 5
^{48}Ca (Low Resolution)	878.7	877.1	879.3	879.9	879.7
^{24}Mg (Low Resolution)	2.793	2.790	2.793	2.800	2.798
Mg/Ca	0.003178	0.003181	0.003176	0.003182	0.003181

RATIO	AVER	STD. DEV.	RSD [%]
Mg/Ca	0.003180	0.0000023	0.07

Table 3: Mg/Ca elemental ratio calculations.

Under routine analytical conditions, an external precision of 0.07% RSD has been achieved for the measurement of both Sr/Ca and Mg/Ca elemental ratios. These values are comparable to previously reported values using a Thermo Scientific ELEMENT[7] and superior to those obtained using quadrupole ICP-MS[1]. The improved precision obtained with the ELEMENT 2 shown in this work can be directly attributed to the characteristic 'flat top' peak shape in low resolution rather than the round shouldered peak of ICP-QMS. An additional factor that influences the precision of ratio measurements by ICP based techniques, is the instability of the plasma (so-called 'plasma flicker'). By using a stabilized sample introduction system the droplet size distribution of particles introduced into the plasma is minimized, significantly reducing 'plasma flicker'.

The comparatively simple analysis procedure presented in this report does not require time consuming sample preparation steps and is therefore suitable especially for a high sample throughput: 5 samples an hour (5 replicate analysis per sample). Because of the high sensitivity of the ELEMENT 2 (> 1 Mcps/ppb Sr) only a small sample amount (~ 2 µg) is required per analysis.

Conclusions

The Thermo Scientific ELEMENT 2 is shown to be a powerful tool for the high precision measurement of Sr/Ca and Mg/Ca elemental ratios in corals. Using solution analysis, Sr/Ca and Mg/Ca elemental ratios in corals were determined with an external precision of 0.07% RSD (1σ). An autosampler enabled fully automatic unattended analysis. The complete measurement procedure is highly efficient and is suitable for high sample throughput.

Rererences

[1] F. Le Cornec, T. Corrége, J. Anal. Atom. Spectrosc. 12 (1997), 969-973

[2] J.W. Beck, R.L. Edwards, E. Ito, F.W. Taylor, J. Recy, F. Rougerie, P. Joannot, C. Henin, Science, 257 (1992), 644-647

[3] D.W. Lea, P.A. Martin, Geochimica et Cosmochimica Acta, 60 (1996), 3143-3149

[4] D.P. Schrag, in press

[5] D.J. Sinclair, L.P.J. Kinsley, M.T. McCulloch, 62 (1998), 1889-1901

[6] S.R. Hart, A.L. Cohen, Geochimica et Cosmochimica Acta, 60 (1996), 3075-3084

[7] Y. Rosenthal, M.P. Field, R.M. Sherrell, Winter Conference on Plasma Spectrochemistry, 1999, Pau, France

[8] T.M. Quinn, D.E. Sampson, Fall AGU, 1998, San Francisco

AN30001_E 08/16C