Application Note: 30002

High Precision Determination of Sr/Ca and Mg/Ca Elemental Ratios in Massive Coral Skeletons

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Key Words

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

Summary

The Thermo Scientific ELEMENT 2, a single collector double focusing sector field ICP-MS, was used for the determination of Sr/Ca and Mg/Ca elemental ratios in microgram samples taken from seasonal growth bands in a coral skeleton (*Diploria strigosa*). Variations in $\delta^{18}O$ values were found to be in good agreement with the results for Sr/Ca and Mg/Ca elemental ratio determinations. As shown in a previous study (Thermo Fisher Scientific Application Note AN30001_E) the ELEMENT 2 provides a higher sample throughput compared to TI-MS while providing precision of better than 0.1% RSD for both Sr/Ca and Mg/Ca elemental ratios. Compared with ICP-AES, major and trace elements can be analyzed simultaneously.

Introduction

The temperature of the ambient sea water during skeletal growth is the determining factor for the elemental ratios of Sr to Ca and Mg to Ca in biogenic carbonates. The shells and skeletons of marine organisms, which have growth banding, therefore allow the reconstruction of past water temperatures. These reconstructions for the aragonitic skeletons of massive corals may span several decades in monthly or shorter temporal resolutions (e.g. Alibert and McCulloch, 1997).

Coral skeletons contain relatively high amounts of Sr and Mg (roughly 0.8% and 0.1%, respectively; Amiel et al., 1973). The accurate measurement of these elements is not a problem of instrumental sensitivity, but one of precision: the relative variabilities in the Sr/Ca ratios are in the order of magnitude of 3%, requiring RSDs better than 0.3%. Mg/Ca ratios are less critical, as the variability is roughly four times that of Sr/Ca (Mitsuguchi et al., 1996). Because sample numbers may easily reach hundreds to thousands, minimal sample preparation and short measurement times are required. Because it is only elemental ratios that are of interest, weighing of the raw sample material is often omitted, which can lead to random concentrations in the sample solutions, which may easily vary by a factor of five.

The determination of trace elements-to-calcium ratios, such as Ba/Ca, U/Ca, and Cd/Ca, on the same sample solutions can also be of interest. These measurements require high sensitivities in order to measure the trace elements, and high precision has to be maintained for widely variable elemental concentrations in the same solution (trace element ratios relative to Ca are >1:105).

In summary, the instrumental requirements are:

- Very high precision for the determination of elemental ratios
- Linearity of response over a wide range of sample solution concentrations
- Simultaneous determination of major and trace elements
- Good long-term stability and reproducibility
- High instrumental sample throughput
- Minimal sample preparation

Until recently, Sr/Ca ratios were typically measured by TIMS (e.g. Beck et al., 1992; Alibert and McCulloch, 1997; Gagan et al., 1998). While TI-MS provides excellent precision and sensitivity, it is expensive, time-consuming, and requires extensive sample preparation. Modern ICP-MS-based methods (e.g. Le Cornec 1999 and Correge, 1997; Sinclair et al., 1998; Rosenthal et. al.) are simpler and more rapid, at the cost of some loss in precision.

Previous studies (Thermo Fisher Scientific Application Note AN30001_E) have shown that the Thermo Scientific ELEMENT 2 provides an improved precision over quadrupole- based ICP-MS systems (< 0.1% RSD for Sr/Ca as well as Mg/Ca elemental ratio determination), which was attributed to the characteristic 'flat top' peak shape in low resolution mode and a high stability sample introduction system.

This report presents the results of the analysis of an annual skeletal layer in a core of a massive reef coral (*Diploria strigosa*). The ELEMENT 2 was used for the determination of Sr/Ca and Mg/Ca elemental ratios in coral skeletons at different coral core depths. In addition, $\delta^{18}O$ values for these samples were available and were correlated with Sr/Ca and Mg/Ca obtained.

Experimental

The coral core investigated was recovered from a living colony of the reef-building species *Diploria strigosa* from a water depth of 11 m northeast of Bermuda.

A stick section of 2 – 3 mm in diameter was sawn from the skeleton and ground in steps of 200 µm. The sample powder produced (typically 400 to 1200 µg per step) was dissolved in 40 ml of 2.5% ultrapure nitric acid (obtained from dilution of 65% HNO_3, purchased from Merck), and diluted 3 to 5-fold using high purity water (18.2 MΩ) and spiked with Ge as an internal standard (100 ng/ml).

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A total of 21 samples were prepared for measurement. Calibration standards used were in the range of 100 – 2000 ng/ml Ca, 1 – 20 ng/ml Sr, and 0.1 – 2 ng/ml Mg.

A CETAC ASX-100 autosampler system was used for fully automatic unattended analysis. The Thermo Scientific ELEMENT 2 ICP-MS parameters are listed in Table 1:

Forward power:	1250 W
Reflected power:	< 2 W
Coolant gas flow:	16 l/min
Sample gas flow:	1.12 l/min
Auxiliary gas flow:	0.85 l/min
Sample introduction:	Stable Sample Introduction System
– Nebulizer	PFA-20 (20 µl/min)
– Spray chamber	Dual Spray Chamber

Table 1: Thermo Scientific ELEMENT 2 ICP-MS parameters.

The ELEMENT 2 measurement parameters used for this analysis are shown in Figure 1. An individual sample took approximately 8.5 minutes (3 replicate analysis per sample) resulting in about 7 samples an hour.

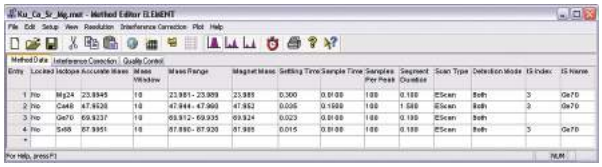

Figure 1: Screen capture of the Method Editor of the Windows® XP software of the Thermo Scientific ELEMENT 2 , showing the nuclides, mass range and a selection of measurement parameters used for the determination of Sr/Ca and Mg/Ca elemental ratios.

Results and Discussion

The results of the Sr/Ca and Mg/Ca elemental ratio determinations and corresponding $\delta^{18}O$ values are summarized in Table 2. The external precision of the Sr/Ca and Mg/Ca elemental ratios were calculated from three determinations of the concentration ratios in the sample. The precision for Sr/Ca and Mg/Ca elemental ratio determination was better than 0.1% RSD. Sr/Ca and Mg/Ca elemental ratios as well as $\delta^{18}O$ values are shown as a function of depth in Figure 2. The ages of the samples increase with depth. Approximately 1 – 1.5 annual cycles are shown. All axes are scaled such that values near the abscissa indicate cooler temperatures.

All three parameters (Sr/Mg, Mg/Ca and $\delta^{18}O$) are strongly dependent on water temperature ($\delta^{18}O$ is also influenced by $\delta^{18}O_{seawater}$).

The fact that these parameters vary in a near sinusoidal pattern indicates that they are recording variability in the sea surface temperature over the course of approximately 1 – 1.5 years (Figure 2). Sr/Ca and $\delta^{18}O$ have a correlation of 0.92 and Mg/Ca and $\delta^{18}O$ have a correlation of -0.63.

SAMPLE NUMBER	SAMPLE DEPTH	SR/CA (MMOL/MOL)	MG/CA (MMOL/MOL)	$\delta^{18}O$ ‰ VERSUS V-PDB
BDA98 2-13	0	9.194	3.893	-3.156
BDA98 2-14	0.2	9.265	3.625	-3.100
BDA98 2-16	0.6	9.246	3.594	-3.241
BDA98 2-17	0.8	9.150	3.760	-3.351
BDA98 2-18	1	9.177	4.040	-3.584
BDA98 2-19	1.2	9.034	4.087	-3.924
BDA98 2-20	1.4	8.970	4.205	-3.924
BDA98 2-21	1.6	8.993	4.029	-3.865
BDA98 2-23	2	9.097	4.001	-3.746
BDA98 2-24	2.2	9.188	4.161	-3.557
BDA98 2-25	2.4	9.227	3.970	-3.356
BDA98 2-26	2.6	9.213	3.860	-3.272
BDA98 2-27	2.8	9.238		-3.016
BDA98 2-28	3	9.248	3.700	-3.089
BDA98 2-29	3.2	9.212	3.684	-3.094
BDA98 2-30	3.4	9.255	3.838	-3.199
BDA98 2-31	3.6	9.189	4.067	-3.267

Table 2: Results of Sr/Ca and Mg/Ca elemental ratio determinations and corresponding $\delta^{18}O$ values.

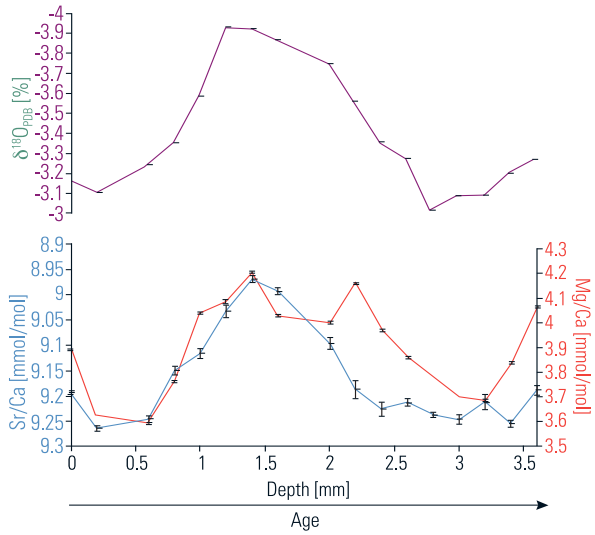

Figure 2: Sr/Ca and Mg/Ca elemental ratios as well as $\delta^{18}O$ values in a coral skeleton. The ages of the samples increase with depth. Values near the abscissa indicate cooler temperatures.

The analytical procedure presented in this work is both simple (very few steps) and rapid (about 7 samples an hour), which guarantees high sample throughput.

Conclusions

The Thermo Scientific ELEMENT 2 is shown to be suitable for the routine analysis of Sr/Ca and Mg/Ca elemental ratios in coral skeletal material. The variation of Mg/Ca and Sr/Ca elemental ratios with coral depth was found to be in good agreement with previous $\delta^{18}O$ measurements. The accuracy and precision (< 0.1% RSD) provided by sector field ICP-MS makes this technique an attractive alternative to TIMS, especially since the sample preparation is shorter and sample throughput therefore higher. The wide dynamic range of the ELEMENT 2, > 9 orders of magnitude, allows the simultaneous determination of major and trace elements in one sample preparation without labor-intensive enrichment or dilution steps. Therefore, sector field ICP-MS allows trace element determinations in biogenic carbonates to be performed routinely, which should be of interest to a variety of geochemical and paleoceanographic studies.

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