

Determination of Uranium to Calcium and Strontium to Calcium Ratios in Corals by Inductively Coupled Plasma Mass Spectrometry†

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A method has been developed to determine Ca (about 40% m/m in corals), Sr (about 1–2%) and U ($3\text{--}5\ \mu\text{g g}^{-1}$) in the same aliquots. All the samples were spiked with ^{45}Sc , ^{89}Y and ^{236}U . None of these isotopes are present in significant amounts in corals. The Ca and Sr were determined using two different approaches. Firstly, ^{45}Sc and ^{89}Y were used as spikes to measure ^{43}Ca and ^{86}Sr , respectively, by the isotope dilution technique (external isotope dilution). It was established that the behaviour of the various elements in the plasma varied from day to day and cannot be modelled with good accuracy (*i.e.*, better than 1%). Therefore, a second approach was developed using ^{45}Sc and ^{89}Y as internal standards. This method yielded extremely good reproducibility within a run and also on a day to day basis, providing the ICP-MS instrument is properly tuned. Values for %RSD of 0.2–0.3% for Ca and Sr measurements were routinely obtained, as were calibration curves with correlation coefficients better than 0.9998. The U was determined by classic isotope dilution. Analyses on a standard solution of coral powder over 5 d yielded %RSDs of 0.25% for Sr:Ca and 0.5% for U:Ca. Accuracy was assessed using the certified reference material CCH-1 and a coral standard (NC20), which were both analysed by ICP-MS and ICP-AES.

Keywords: Inductively coupled plasma mass spectrometry; calcium carbonate; palaeothermometry; calcium; strontium; uranium

Corals secrete a skeleton of aragonite (CaCO_3) in which some trace elements such as Sr, U and Mg appear to be incorporated as a function of water temperature.^{1–3} Thus, determination of Sr:Ca, U:Ca and Mg:Ca ratios in fossil corals can provide information on past sea surface temperatures (SST). This information is crucial to provide climate modellers with quantitative data and for a better understanding of climatic change through time. However, these three tracers have very contrasting concentrations in corals (about $8000\ \mu\text{g g}^{-1}$ for Sr, $1100\ \mu\text{g g}^{-1}$ for Mg and $3\ \mu\text{g g}^{-1}$ for U). Their rates of change with respect to temperature are also different, about 0.9% per °C for Sr:Ca, 3.5% per °C for Mg:Ca and 4% per °C for U:Ca. Magnesium is fairly abundant in corals, and shows variations which can be easily quantified with ICP-AES. Strontium and U are different, because Sr is abundant but varies little whereas U is just the opposite. As a consequence, all the pioneering work on Sr:Ca and U:Ca palaeothermometry has been carried out so far with thermal ionisation mass spectrometry (TIMS), which gives good precision (<0.1%) but is expensive and slow. Shen and Dunbar⁴ have developed a fast method to measure U by isotope dilution ICP-MS but Ca determinations were made separately by FAAS. The present work proposes a new method developed on an ICP-MS

instrument to measure Ca, Sr and U precisely in the same aliquot. The main advantage of ICP-MS over TIMS is the large sample output attainable with ICP-MS (between 50 and 100 samples per day). The present work also demonstrates that the external isotope dilution method recently developed by Lea and Martin⁴ is not a viable option to measure Ca and Sr with good precision.

EXPERIMENTAL

Instrumentation

The ICP-MS instrument used in this study is a VARIAN UltraMass (Varian, Les Ulis, France). Samples are introduced via a V-groove nebulizer and an inert Sturman-Masters spray chamber. The sample introduction assembly is always at constant room temperature because it is mounted outside the torch box. Thus, any possible drift effect caused by reflected heat from the plasma compartment is eliminated. Ions are detected by a discrete dynode electron multiplier (DDEM) detector. All parameters, such as xyz positioning of the plasma relative to the sampler cone, rf power, ion lens voltages and all plasma gas flows (Table 1), are computer-controlled.

Reagents

High purity de-ionised water ($18.2\ \text{M}\Omega\ \text{cm}$) was obtained from a Millipore Milli-Q₁₈₅ Plus unit (Millipore, Villiers-le-bel, France). All working standard solutions were prepared by appropriate dilution of mono-elemental $1000\ \mu\text{g ml}^{-1}$ certified stock solutions (Spex, Longjumeau, France) in 2% nitric acid (Suprapur 65% nitric acid, Merck, Darmstadt, Germany). The ^{236}U uranium spike was purchased from Amersham (Les Ulis, France). To validate the method, a sedimentary rock reference material, CCH-1 (Geology, Petrology and Geochemistry

Table 1 Acquisition parameters and plasma operating conditions for Ca, Sr and U

Method	Ca, Sr	U
<i>Acquisition parameter —</i>		
Scan mode		Peak hopping
Spacing		0.1
Points per peak		1
Dwell time/ μs	5000	10000
Scans per replicate	100	250
Number of replicates		3
Detector voltage/V		2200
<i>Plasma parameter —</i>		
Plasma gas flow/ l min^{-1}	16	18
Intermediate gas flow/ l min^{-1}	1.15	1.10
Aerosol carrier gas flow/ l min^{-1}	0.78	0.82
Sampling depth/mm	5	6
Power/kW	1.33	1.35
Sample uptake rate/ ml min^{-1}		1

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Laboratory, Liège University, Belgium), and an in-house coral standard labelled NC20 were used. All standards and samples were prepared by weighing reagents with a precision of 0.1 mg and stored in pre-cleaned polypropylene or Teflon bottles.

Sample Preparation

Samples consist of calcium carbonate powder (typically less than 1 mg) drilled from a coral slab. This powder is dissolved in 6 ml of 2% nitric acid (Suprapur 65% nitric acid, Merck) which contains all the trace elements necessary to the analysis. On average, samples contain $70 \mu\text{g g}^{-1}$ of Ca, $1.5 \mu\text{g g}^{-1}$ of Sr and 0.5 ng g^{-1} of U.

Development of the Method

The purpose of this work was to measure, with the same instrument and on the same aliquots, Ca, Sr and U. However, when developing the method, two major problems had to be dealt with: (i) Ca (about 40% m/m in corals) and Sr (about 1–2%) are major elements in corals, whereas U is present at the trace level (about $3\text{--}5 \mu\text{g g}^{-1}$); and (ii) these three elements have very different mass to charge ratios (m/z) and therefore a compromise in the optimisation of instrumental parameters, especially ion lenses, had to be found. The ICP-MS operating conditions were selected in order to obtain the best sensitivity for U coupled with the best precision for Ca and Sr. However, although the method for Ca and Sr gave relatively good precision for U, it was decided to develop a separate method specifically for this element. The U method allows the %RSD to be lowered by a factor of 2–3 for this element compared with the previous method.

Choice of Isotopes

The most abundant isotope of Ca, ^{40}Ca , has an isobaric interference with ^{40}Ar and therefore cannot be measured using ICP-MS. In any case, because of the high concentration of Ca that has to be quantified ($70 \mu\text{g g}^{-1}$ on average), even ^{44}Ca and ^{42}Ca are still too abundant (2.086 and 0.647% of the total Ca, respectively). Therefore, ^{43}Ca and ^{48}Ca which have an abundance of 0.135 and 0.187%, respectively, were selected. There is a small interference of doubly charged ^{86}Sr on ^{43}Ca , therefore the operating conditions of the instrument were adjusted to minimise this. Each day, the count rate for $^{86}\text{Sr}^{2+}$ was measured and the count rate for ^{43}Ca eventually corrected. No evidence was found for a ^{43}Ca - ^{43}Ca interference on ^{86}Sr . Results given by the two measured isotopes of Ca were compared for accuracy and reproducibility.

For quantification of Sr, ^{88}Sr could not be used because the count rates were well over the saturation threshold of the detector, hence ^{86}Sr was chosen (with a natural abundance of 9.86%).

The most abundant isotope for U was measured *i.e.*, ^{238}U .

Optimisation of ICP-MS Instrument

applied to the first lens had a great influence on the stability of the Ca and Sr count rates, and therefore this particular lens was fine-tuned each day.

Sr: Ca Measurement

To measure Ca and Sr in corals, two approaches were tried, each involving the addition to the samples of the mono-isotopic elements ^{45}Sc and ^{89}Y . Neither Sc nor Y are present in significant amounts in corals. Calcium and Sc are very close in mass and first ionisation energy and show a similar behaviour with time in the plasma. The same is true of Sr and Y. The 'external isotope dilution' analytical method proposed by Lea and Martin was tried first,⁵ then, the present method was developed which is a slight variation of the internal standard method.

'External isotope dilution'

In their article,⁵ Lea and Martin claimed that ^{45}Sc and ^{89}Y can be used to quantify Ca and Sr, respectively, by isotope dilution. This method was tested, and although the following discussion will focus on Ca and Sc, the same conclusions apply to Sr and Y.

To perform isotope dilution on Ca with another element such as Sc, the behaviour in the plasma of the different isotopes involved had to be investigated in order to try to answer some key questions. (i) Do Sc and Ca ionise to the same extent in the plasma? (ii) If there is a difference in ionisation, can it be quantified? (iii) Is this difference constant or is it dependent on factors such as the concentration of Ca?

Pure Ca (between 30 and $90 \mu\text{g g}^{-1}$), Sr (between 1 and $2 \mu\text{g g}^{-1}$) and Sc-Y (100 ng g^{-1}) standards were run alternately with mixed Ca-Sc-Sr-Y standards with similar concentrations, on four different days during a two week period. The count rates per ng g^{-1} for ^{43}Ca , ^{48}Ca , ^{45}Sc , ^{86}Sr and ^{89}Y were calculated and compared. Several important facts can be noted.

1. Calcium does not interfere with the ^{45}Sc signal. The Sc counts are identical in ultrapure HNO_3 , *i.e.*, blanks and in pure Ca standards.

2. The difference in counts per second (cps) per ng g^{-1} between ^{43}Ca and ^{45}Sc expressed in % over ^{43}Ca as a function of Ca concentration is shown in Fig. 1. The same treatment was applied to the pairs ^{48}Ca - ^{45}Sc and ^{86}Sr - ^{89}Y , in Fig. 1(b) and (c), respectively. Ideally, if Sc is to be used for isotope dilution of Ca, the percentage difference in cps per ng g^{-1} between ^{43}Ca and ^{45}Sc should be independent of the Ca concentration. This is clearly not the case. The higher the concentration of Ca, the lower the difference calculated between ^{43}Ca and ^{45}Sc , and also between ^{48}Ca and ^{45}Sc . The present experiment also indicates that for the same standard, large fluctuations of this difference occur on a day to day basis, which makes it difficult, if not impossible, to model.

The relationship linking Ca concentration to the difference in count rates between ^{43}Ca and ^{45}Sc appears to be linear. The equation of the daily regression line is given and demonstrates

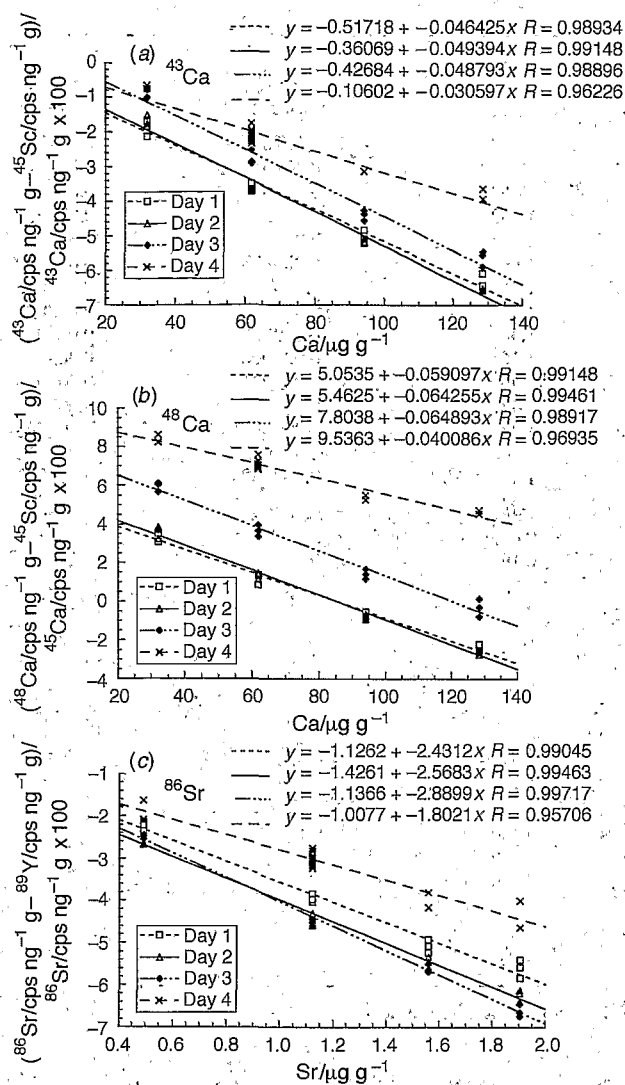


Fig. 1 (a) Difference in cps per ng g⁻¹ between ⁴³Ca and ⁴⁵Sc expressed in % over ⁴³Ca as a function of Ca concentration; (b) difference in cps per ng g⁻¹ between ⁴⁸Ca and ⁴⁵Sc expressed in % over ⁴⁸Ca as a function of Ca concentration; and (c) difference in cps per ng g⁻¹ between ⁸⁶Sr and ⁸⁹Y expressed in % over ⁸⁶Sr as a function of Sr concentration.

However, in classical internal standardisation, small differences in the concentration of Sc and Y between the standard solutions and the samples, owing to differences in preparation, are not accounted for. Furthermore, mass bias, which can vary substantially in the mass range of Ca of interest, cannot be corrected. The method developed eliminates these two problems and yields highly accurate and reproducible Ca and Sr measurements. Scandium and Y were added to the four standard stock solutions and to the samples at a concentration of 100.0 ng g⁻¹. This value was chosen because it yields target ratios for ⁴³Ca: ⁴⁵Sc, ⁴⁸Ca: ⁴⁵Sc and ⁸⁶Sr: ⁸⁹Y close to unity. These ratios were corrected for an instantaneous mass bias effect (measured with ⁴³Ca: ⁴⁸Ca for Ca and ⁸⁶Sr: ⁸⁷Sr for Sr), and normalised to a true internal standard concentration of 100.0 ng g⁻¹. Four multi-element standards were run and calibration lines linking Ca concentration to ⁴³Ca: ⁴⁵Sc and ⁴⁸Ca: ⁴⁵Sc [Fig. 2(a)] and Sr concentration to ⁸⁶Sr: ⁸⁹Y [Fig. 2(b)] were calculated. The correlation coefficients (R) were always higher than 0.9998 for Ca and Sr. As many parameters, such as configuration and properties of the cones, properties of the lenses, efficiency of sample introduction system and plasma conditions, can change the sensitivity and the rate of interfering species, calibration

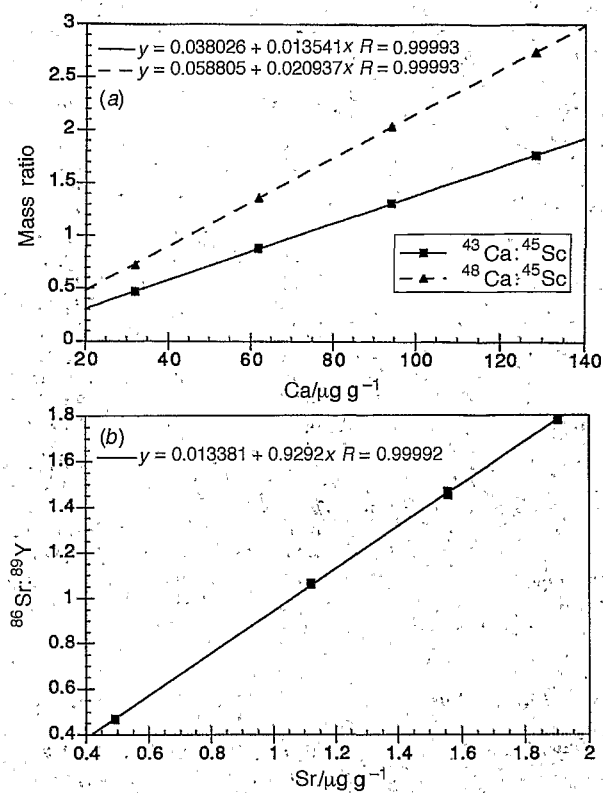


Fig. 2 (a) Mass ratios versus Ca concentration for four multi-element standards. The regression lines and their equations are also shown. (b) ⁸⁶Sr: ⁸⁹Y versus Sr concentration for four multi-element standards. The regression line and its equation are also shown.

curves were calculated each day. The output of this method is 20 analyses per hour with a dilute nitric acid wash of 1 min 30 s in the fast sample uptake rate between each sample. Calcium and Sr concentrations in coral samples were then derived from the equation of the regression lines [see Fig. 2(a) and (b)], and the Sr:Ca molar ratio in the sample calculated.

U: Ca Measurement

Uranium was measured by classic isotope dilution after addition of a ²³⁶U spike to the 2% nitric acid used to dissolve the coral samples. The ²³⁵U: ²³⁸U of a solution of known isotopic abundance, NBL SRM U500 (New Brunswick Laboratories, USA), was measured each ten samples to assess the mass bias. This mass discrimination effect was always less than 1% per *m/z* value and the variation after 3 h did not exceed 0.5%. The RSDs for ²³⁸U: ²³⁶U calculated on three successive replicates in coral samples at a level of 0.3 ng g⁻¹ in ²³⁸U were around 1%. The U content in the sample was obtained directly from ²³⁸U: ²³⁶U corrected by mass bias and multiplied by the ²³⁶U concentration and factor of natural abundance of ²³⁸U. Then the U:Ca molar ratio was calculated from the Ca concentration found previously. The output of this method is around 25 samples per hour and no calibration is necessary.

RESULTS AND DISCUSSION

The ICP-MS method described herein can be compared with other techniques of quantification such as TIMS or ICP-AES, in terms of sample output and accuracy.

Table 2 Reproducibility over 5 d, on coral standard NC20

A. Ca, Sr and Sr:Ca—					
Date	⁴³ Ca/μg g ⁻¹	⁴⁸ Ca/μg g ⁻¹	⁸⁶ Sr/μg g ⁻¹	Sr: ⁴³ Ca/ mmol mol ⁻¹	Sr: ⁴⁸ Ca/ mmol mol ⁻¹
17/09/96	74.22	74.20	1.469	0.009051	0.009054
	74.36	74.34	1.466	0.009015	0.009018
	74.16	74.14	1.463	0.009026	0.009028
18/09/96	74.43	74.08	1.462	0.008988	0.009030
	74.24	73.90	1.467	0.009036	0.009078
	74.60	74.26	1.468	0.008998	0.009040
24/09/96	74.21	74.51	1.466	0.009039	0.009003
	74.14	74.43	1.468	0.009059	0.009022
	74.12	74.41	1.468	0.009058	0.009022
26/09/96	73.91	73.92	1.465	0.009066	0.009065
	74.19	74.21	1.465	0.009031	0.009030
	74.26	74.28	1.472	0.009067	0.009066
9/10/96	74.22	74.46	1.472	0.009074	0.009044
	74.13	74.37	1.467	0.009052	0.009022
	74.14	74.39	1.467	0.009052	0.009022
Mean	74.22	74.26	1.467	0.009041	0.009036
s	0.16	0.19	0.003	2.5 × 10 ⁻⁵	2.1 × 10 ⁻⁵
RSD (%)	0.21	0.25	0.19	0.28	0.23
t-test value*		0.6046			
Student's		2.0484			
t-value (α = 5%)					

B. Ca, U and U:Ca—			
Date	Ca/μg g ⁻¹	U/ng g ⁻¹	U: Ca/μmol mol ⁻¹
17/09/96	74.23	0.5054	1.155
18/09/96	74.08	0.5072	1.161
24/09/96	74.45	0.5091	1.160
26/09/96	74.13	0.5109	1.169
09/10/96	74.41	0.5090	1.160
Mean	74.26	0.5083	1.161
s	0.16	0.0021	0.005
RSD (%)	0.22	0.41	0.43

* The t-test indicates that results from ⁴³Ca and ⁴⁸Ca are not significantly different at the 5% risk level.

Sample Consumption and Output

With the TIMS technique, a very small amount of sample is sufficient for Sr:Ca determination: between 20 and 50 μg of material.^{1,2,6} For the determination of U, samples weighing around 2 mg are generally used² because of the low concentration of U and the chemical treatment necessary prior to analysis.

For ICP-MS determination, the three elements of interest can be measured by dissolving 1 mg of coral in about 6 ml of 2% nitric acid. Since no special treatment is needed after the coral powder has been dissolved, preparation time is much shorter than for TIMS.

A second advantage of ICP-MS is the large sample output in comparison with TIMS. On average, 50–80 samples can be analysed daily for Sr, Ca and U in the manual mode, and up to 100 if an autosampler is available. On the contrary, TIMS is very slow, and in the best case, a Sr–Ca–U determination takes at least 2 h. Therefore ICP-MS will be cheaper and is a particularly interesting technique to generate series of sea surface temperatures over long periods of time.

Short and Long Term Precision

The short (repeatability) and long term stability (reproducibility) over several days are two essential factors for work on corals for two reasons. Firstly, the rate of change of Sr:Ca per °C is small (about 0.9%) and the yearly variations in sea

therefore extremely important to obtain a good day to day reproducibility.

The repeatability of the ICP-MS method was assessed by measuring a standard solution for a 3 h period. The %RSD for ⁴³Ca: ⁴⁵Sc, ⁴⁸Ca: ⁴⁵Sc and ⁸⁶Sr: ⁸⁹Y were all less than 0.3% (Fig. 3) while the RSDs of the counts per second for ⁴³Ca, ⁴⁸Ca and ⁸⁶Sr for the same period were 4.0, 3.8 and 3.9%, respectively.

To evaluate the reproducibility of the ICP-MS method, the same coral (*i.e.*, NC20) was analysed on 5 d over a 3 week period (Table 2A and B). Each day, Sr, Ca and U were determined three times. The Sr:Ca values were calculated from calibration equations for ⁴³Ca and ⁴⁸Ca, respectively. The differences between the two results are not significant (Table 2A) and are well below the precision of calibration

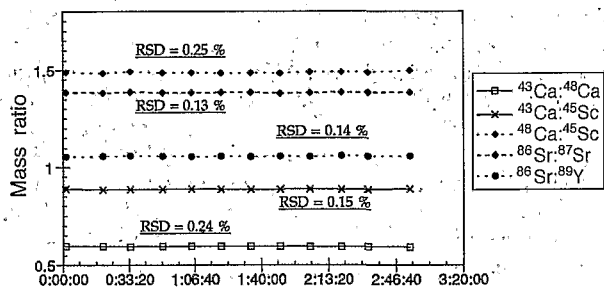


Table 3 Comparison of Ca and Sr determinations by ICP-MS and ICP-AES for reference carbonate CCH-1 and for coral standard NC20

Parameter	Certified value	ICP-MS	ICP-AES
<i>CCH-1</i> —			
Ca (%)	37.25	37.01	37.74
Number of analyses		54	3
<i>NC20</i> —			
Ca/ $\mu\text{g g}^{-1}$		83.69	84.18
Sr/ $\mu\text{g g}^{-1}$		1.654	1.653
Sr:Ca/ mmol mol^{-1}		0.0090394	0.0089825
Number of analyses		9	3
<i>t</i> -test value* (on Sr:Ca)			1.381
Student's <i>t</i> -value ($\alpha=5\%$)			2.228

* The *t*-test indicates that results from ICP-MS and ICP-AES are not significantly different at the 5% risk level.

curves. The precisions on U:Ca are lower than on Sr:Ca. However, as the amplitude of the U:Ca variations as a function of SST is higher, the precision on SST will be the same or better. In the literature, the short and long term precision reported for TIMS methods is generally better than 0.1% for less than eight measurements.^{1,2}

The precision of the method developed here for ICP-MS is certainly good enough for palaeothermometry work on coral. Coupled with the high sample output attainable with ICP-MS, it indicates that this instrument has the capability to replace TIMS as the best technique for generating long term records of palaeotemperatures.

Accuracy

The accuracy of the ICP-MS method was assessed in various ways. Coral standard NC20 was analysed with ICP-AES to check for Ca and Sr concentrations (Table 3). The reference carbonate material CCH-1 was also analysed. In both cases, the values generated by ICP-MS were consistent with those obtained with ICP-AES or other techniques.

CONCLUSION

A rapid method has been developed to determine precisely Ca, Sr and U in calcium carbonates. Although this method was used for palaeothermometry on aragonitic corals, it can be equally applied to studies of calcitic organisms, such as ostracods or foraminifers. Furthermore, preliminary results indicate that other elements of interest to palaeoceanography (Mg and Ba in particular) can be determined at the same time by isotope dilution, simply by introducing the appropriate spikes in the nitric acid prior to dissolving the coral powder.

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