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High precision measurements of Mg/Ca and Sr/Ca ratios in carbonates by cold plasma inductively coupled plasma quadrupole mass spectrometry

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Abstract

We present a new high precision analytical method for the determination of Mg/Ca and Sr/Ca ratios in carbonates using an inductively coupled plasma quadrupole mass spectrometer (ICP-QMS) with a 650-W cold plasma technique and a desolvation introduction system. Signal intensities are detected in pulse-counting mode and Mg/Ca and Sr/Ca ratios are calculated directly from intensity ratios of ²⁴Mg/⁴³Ca and ⁸⁶Sr/⁴³Ca using external matrix-matched standards for every 4–5 samples to correct for instrumental mass discrimination and low-frequency ratio drift. Significant matrix effect of Ca content on Mg/Ca determination (-0.018 Mg/Ca (mmol/mol)/[Ca] (ppm)), can be overcome by diluting [Ca] to 6-8 ppm in the sample solution or using an empirical correction. The Sr/Ca ratio affects the Mg/Ca determination, with a factor of -0.32% Mg/Ca per mmol/mol. This is mainly caused by the influence of doubly charged ⁸⁶Sr, which biases the intensity measurement of the ⁴³Ca⁺ ion beam. This effect results in a trivial offset of less than 0.1% on Mg/Ca measurements for Quaternary foraminiferal and coral samples. The internal precision of our method ranges from 0.1 to 0.2%. Replicate measurements made on standards and samples show long-term external uncertainties (2σ) of Mg/Ca=0.84% and Sr/Ca=0.49%. The minimum sample size requirement is only 3.5 μ g of carbonate. The application of this newly developed technique on the planktonic foraminifera Globigerinoides ruber from a core recovered in the southern South China Sea yields a glacial-interglacial difference in sea surface temperature (SST) of 3 °C. Three-year coral Sr/Ca data suggest that the seasonal SST ranged from 22.6–23.8 °C in winter to 26.9–27.9 °C in summer in Nanwan, south Taiwan, during 2000-2002. The coral-Sr/Ca inferred SSTs in 2002 match well with instrumental records, which demonstrates the validity of this ICP-QMS method.

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1. Introduction

The Mg and Sr contents of natural carbonates are widely used as proxies in studies of environmental and climatic change. Mg/Ca ratios in foraminifera and Sr/Ca

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ratios in corals, for example, have been used to reconstruct oceanic thermal conditions in the past (e.g., Beck et al., 1992; Nürnberg et al., 1996; Gagan et al., 2000; Elderfield and Ganssen, 2000; Lea et al., 2000; Hendy et al., 2002; Shen et al., 2005; Yu et al., 2005a; Lin et al., 2006; Steinke et al., 2006). The magnitudes of these signals are usually small; only 9%/°C for foraminiferal Mg/Ca, and 0.8%/°C for coral Sr/Ca thermometers (e.g., Shen et al., 1996; Gagan et al., 2000; Dekens et al., 2002; Anand and Elderfield, 2003). Therefore, the establishment of high precision analytical techniques plays a critical role in the application of these geochemical tracers.

High precision measurements with an uncertainty of better than 0.1% can be achieved using isotope dilution thermal ionization mass spectrometry (ID-TIMS; Beck et al., 1992; Shen et al., 1996). However, certain limitations, including slow sample throughput and high cost, restrict its broad application. ID-TIMS cannot likely satisfy the increasing demand for high sample throughput required by high-resolution and long-term studies. Analytical precisions of 0.4-4% have been achieved by fast analytical techniques, including inductively coupled plasma atomic emission spectroscopy (ICP-AES; Schrag, 1999; de Villiers et al., 2002; Sun and Sun, 2003; Wara et al., 2003), isotope dilution inductively coupled plasma quadrupole mass spectrometry (ID-ICP-QMS; Le Cornec and Correge, 1997; Lea et al., 1999; Sun and Sun, 2002) and ICP-sector field (SF)-MS (Rosenthal et al., 1999; Marchitto, 2006).

The ICP-QMS technique offers some advantages, such as rapid multi-element analysis, a low detection limit, and high selectivity. In contrast to the flat-topped peak shape of ICP-SF-MS method, however, the Gaussian peak shape characteristic of the ICP-OMS method places certain limits on measurement precision. A recently developed method by Yu et al. (2005b) offers long-term 2 precisions of 2.8% and 1.8% for Mg/Ca and Sr/Ca, respectively. Even with isotope dilution techniques, the analytical errors range from 0.5-1.3% (Le Cornec and Correge, 1997; Lea et al., 1999; Sun and Sun, 2002). Additionally, there are several factors that affect the measurement precision of low-mass elements in carbonates by ICP-QMS techniques, including (a) spectral background from polyatomic interferences (Vanhaecke et al., 1996; Montaser, 1998), (b) mass discrimination and ratio drift, (c) chemical matrix effects, (d) Ca deposition on sampling cones, and (e) interference of doubly-charged ions of 86Sr on the determination of the ⁴³Ca⁺ intensity (Horlick et al., 1985; Wilson et al., 1987; Ross and Hieftje, 1992; Vanhaecke et al., 1992; Pupyshev and Semenova, 2001;

Yu et al., 2005b). The above-mentioned issues are addressed in this study. We present an ICP-QMS method using a 650-W cold plasma technique for determining the Mg/Ca and Sr/Ca ratios in carbonates. Examples given include coral and planktonic foraminiferal samples.

2. Experimental

2.1. Labware, standards and sample preparation

Polyethylene (PE) bottles and vials were cleaned with 3 N boiling guaranteed reagent (GR) grade HNO₃ (Merck and CO. Inc.) and hot Milli-Q Element water. Teflon bottles and beakers were cleaned with 1:1 GR HNO₃. Teflon containers were cleaned in acid baths (Edwards, 1988; Shen et al., 2003). Ultrapure HNO₃ (Seastar Chemicals) was used for chemistry. All chemical procedures were performed in a clean room with class-100 working bench at the Department of Geosciences, National Taiwan University.

Primary Mg/Ca and Sr/Ca standards were prepared gravimetrically in Teflonware using high purity metal magnesium chips (99.99%, High-Purity Standards), calcium carbonate powder (>99.999%, Sigma-Aldrich Inc.), and strontium carbonate powder (99.995%, Sigma-Aldrich Inc.). Impurities of Mg and Sr from the calcium carbonate powder caused an insignificant bias of less than 0.01% for Mg/Ca and Sr/Ca ratios in the primary standard solution. Secondary standards were prepared gravimetrically by mixing commercial high purity 1000-ppm Mg, Ca, Sr, and standard solutions of Al, Mn, and Fe (High-Purity Standards) in Teflonware. Working standards contained 7 ppm [Ca] and were used for routine measurements to quantify elemental ratios in samples. These working standards were prepared by diluting secondary mixed standards and were calibrated with primary standards.

A fossil *Porites* coral core was drilled from Xisha Island, northwest South China Sea (16°50' N, 112°20' E; Sun et al., 1999), and a living *Porites* coral head, NW940101, was collected from the water intake channel of the nuclear power plant in Nanwan (21°58' N, 120°42' E), southern Taiwan, in 1994 (Shen et al., 1996).

ID-TIMS Sr/Ca data of monthly-resolved subsamples of Xisha and Nanwan corals have been measured by Shen et al. (1996) and Chiu (1999) for comparison with ICP-QMS values. Three-year bi-weekly ICP-QMS Sr/Ca data were analyzed from a modern *Porites* coral head, NW0310, collected from the same site as NW940101. Subsamples were ultrasonicated and dissolved with 1% HNO₃.

Tests of the planktonic foraminifera, *Globorotalia menardii*, from marine sediment core ODP1115B (09°11′ S, 151°34′ E; water depth of 1148.8 m) were dissolved to provide a foraminiferal reference solution, FORAM-GM, after treating with a cleaning process (Shen et al., 2001). Tests of the planktonic foraminifera, *Globigerinoides ruber*, were selected from core depths of 12.5–900 cm from core MD01-2390 (06°38′ N, 113°25′ E; water depth of 1545 m; Steinke et al., 2006). Samples were cleaned in successive steps, following the cleaning protocol developed by Barker et al. (2003), and dissolved with 1% HNO₃.

A range of 6-8 ppm [Ca] in the solution of coral and foraminiferal samples was diluted with 1% HNO₃ in an additional acid-cleaned PE or Teflon vial for routine ICP-QMS analysis. All measurements were done within 24 h after carbonates were dissolved with 1% HNO₃ to avoid Mg contamination, leached from plastic vials.

2.2. Instrumentation

Measurements of Mg, Ca, and Sr were performed on an ICP-QMS, Agilent Technologies Agilent 7500s, equipped with an electron multiplier. The spectral interferences at mass intervals of interest with different radio frequency (RF) power levels were screened. A cold plasma technique with a RF power of 650 W was chosen to effectively minimize spectral interference. Plasma and auxiliary Ar gas flows were set at 15 L/min and 1 L/min, respectively. Peak width (10%) was 0.7 amu.

For an ICP-MS equipped with a general cyclonic spray chamber, a high Ca concentration of 50-200 ppm needs to be introduced (e.g., Sun and Sun, 2002; Yu et al., 2005b). At these concentrations, data quality can be adversely affected by Ca deposition on sampling cones (Yu et al., 2005b). In addition, high concentrations require a large sample size of 50-100 µg carbonate. These problems were effectively reduced by using a desolvation nebulization device, a Cetac MCN6000, as the sample introduction system. This step decreased [Ca] from 100 ppm to 7 ppm. This dry introduction system provides not only a 5-10-fold enhancement in sensitivity, but also reduces spectral interference caused by polyatomic species of H, N, O and Ar, and matrix effects (Shen et al., 2002). Sample Ar flow was set at 0.40-0.44 L/min and sweep Ar gas flow at 2.7 L/min. No N2 gas flow was introduced. Temperatures of the spray chamber and desolvator were set at 80 °C and 160 °C, respectively. The MCN6000 spray chamber and micro-nebulizer were removed and washed manually every 2-3 h to clean accumulated droplets and reduce instrumental memory blank.

Measurements of standard solutions were duplicated to characterize analytical precision, mass discrimination, and ratio drift. Standards with identical elemental ratios and various Ca concentrations of 1–10 ppm were first tested to assess the interference of [Ca] level on Mg/ Ca and Sr/Ca measurements. Standards with constant Mg/Ca ratios and different Sr/Ca ratios were used to differentiate the matrix effect of Sr/Ca ratios on the Mg/ Ca ratio, and vice versa. A 7 ppm [Ca] solution was sequentially determined for routine measurement.

The nuclides of ²⁴Mg, ⁴³Ca, and ⁸⁶Sr were selected to determine Mg/Ca and Sr/Ca ratios since the intensities of these ion beams have high ranges of 0.2- 1.5×10^6 counts per second (cps). These intensities provide high precision data and can be detected in pulsecounting mode to avoid the additional uncertainty of cross-calibration with analog mode. A count rate of 1.0×10^6 cps of 43 Ca⁺ was generated using a 7 ppm [Ca] solution at a sample uptake rate of 40 µl/min. Typical ion beams of ${}^{24}Mg^+$ and ${}^{86}Sr^+$ were 1.5×10^6 cps and 1.2×10^6 cps for coral and 1.0×10^6 cps and 0.2×10^6 cps for planktonic foraminifera, respectively. Measurement times were 5 min for each sample, followed by a wash step using 1% HNO₃ for 3 min to reduce instrumental memory blank. Within-run precisions for Mg/Ca and Sr/ Ca ranged from 0.1-0.2%. A data set of background counts in the last 2-minute washout interval and signal counts during the last 3.5-minute interval of measurement were collected for development of an off-line data reduction process using an Excel spreadsheet and a Visual Basic macro program developed by Shen et al. (2002). Mg/Ca and Sr/Ca ratios were calculated off-line from intensity ratios using a standard-bracketing linear interpolation method. The nuclides, ²⁷Al, ⁵⁵Mn, and ⁵⁷Fe, were also monitored to assess cleaning efficacy for labware and carbonate samples. The detailed data

Table 1 Data acquisition method

Measurement mode	Peak hopping				
Detection mode	Pulse-counting				
Points per peak	1				
Analysis time (min)	5				
Sample volume (µL)	200				
Isotopes	Integration time (s)				
²⁴ Mg	0.02				
²⁷ Al	0.005				
⁴³ Ca	0.02				
⁵⁵ Mn	0.005				
⁵⁷ Fe	0.005				
⁸⁶ Sr	0.04 (for foraminifer), 0.02 (for coral)				

Table 2 Spectral background for isotopes of Mg, Ca and Sr with different RF power levels under the individual optimization conditions with 1% HNO₃^a

Element	Mass (m/z)	Spectral background (cps) with RF power levels			
		600 W	800 W	1100 W	1300 W
Mg	24	280	710	920	2100
	25	40	90	120	280
	26	460	1000	7000	7000
Ca	42	1400	2700	2100	2950
	43	220	380	460	530
	44	9600	11,000	8400	11,500
	46	80	150	300	360
	48	400	1000	900	1900
Sr	84	750	1500	1400	2500
	86	260	550	540	830
	87	250	400	260	370
	88	160	210	180	220

^a These optimal conditions were tuned with 1-ppm-Ca standard solution by adjusting Ar flow rates and sampling depth.

acquisition method is shown in Table 1. All errors are two standard deviations (2σ) unless otherwise noted.

3. Results and discussion

3.1. Spectral interferences and blanks

Different ICP-MS instruments equipped with different introduction systems display a range of spectral background levels. For example, the interference at m/z = 24 is 200–500 cps using either a normal (1200 W) or cold (600 W) plasma condition for an Elan 6000 ICP-MS with Scott-type spray chamber (Tanner, 1995). Spectral backgrounds for isotopes of Mg. Ca and Sr at different RF power levels under the individual optimization conditions using 1% HNO₃ in this ICP-QMS system are shown in Table 2. The optimization conditions were adjusted using a 1 ppm [Ca] secondary standard solution by changing the flow rates of cool Ar, auxiliary Ar and sample Ar, sampling depth, and sweep Ar flow of the MCN6000. The interference decreases dramatically with low RF power. Background levels decrease from 2100 cps at 1300 W to only 280 cps at 600 W at m/z=24; while the intensity of the ²⁴Mg⁺ ion beam drops only \sim 50%. Consequently, an RF power of 650 W with a steady plasma condition was used for routine measurement. The background counts are about 200, 200, and 300 cps at m/z=24, 43 and 86, respectively; and less than 0.05% of the primary signals. Instrumental blanks, from the residuum of previously analyzed samples, ranged from 100 to 400 cps,

corresponding to only 0.02-0.04% of the ion beams of $^{24}Mg^{+}$, $^{43}Ca^{+}$ and $^{86}Sr^{+}$. The overall background level, including polyatomic interferences and instrumental blanks, is less than 0.07%. These small sources of noise were all corrected in the data reduction process. At a [Ca] of ~ 10 ppm, significant Mg contamination leached from plastic ware was reported by Wara et al. (2003). The background counts in acid-cleaned vials using 1% HNO₃ at m/z=24 increased from 200-300 cps to 5000 cps in one week. This leached Mg could cause a bias of $\sim 1\%$ on Mg/Ca measurements at a [Ca] of 7 ppm. No leached Ca and Sr were found in the plastic ware. Carbonate samples were analyzed within 24 h after dissolution in cleaned PE vials to avoid significant Mg contamination. No Mg contamination was found in acid-cleaned Teflonware, which can be used as substitutes in chemistry.

Intensity of the ${}^{43}Ca^+$ ion beam is biased by the formation of ${}^{86}Sr^{2+}$. A level of 0.15–6% of ${}^{86}Sr^{2+}$ was found in previous studies (Horlick et al., 1985; Wilson et al., 1987; Ross and Hieftje, 1992; Vanhaecke et al.,



Fig. 1. Ratio drift in (a) Mg/Ca and (b) Sr/Ca over a 2-hour measurement experiment (black circles). The magnitude is $\sim 2\%$ for Mg/Ca. A standard-bracketing method effectively removes the low-frequency drift and gives short-term external precisions of 0.5% for Mg/Ca and 0.4% for Sr/Ca (open circles).



Fig. 2. Matrix effect of [Ca] on (a) Mg/Ca and (b) Sr/Ca measurements. The matrix effect of [Ca] is noticeable on Mg/Ca by a factor of -0.018 Mg/Ca(mmol/mol)/[Ca] (ppm), but negligible for Sr/Ca. Four duplicated measurements, on the 14th, 21st, 25th, and 28th of April, 2004, are shown as gray symbols, and the average values as open dots with 2σ .

1992). In our ICP-QMS system, 3% of this doubly charged ion is observed.

3.2. Mass discrimination and ratio drift

Mass discrimination (or mass bias) occurs for all kinds of ICP systems and limits the analytical precision and accuracy (Rosenthal et al., 1999; Schrag, 1999; Rehkamper et al., 2001; Shen et al., 2002). In this ICP-OMS system, isotopic mass discriminations are 8% for Mg, 6% for Ca and 4% for Sr, by comparing the measured isotopic ratios to the true values for each element. One example of low-frequency drift of measured elemental ratios is shown in Fig. 1. Mg/Ca ratios varied from 5.40 mmol/mol to 5.52 mmol/mol, and Sr/Ca ratios ranged from 1.469 mmol/mol to 1.481 mmol/mol, in 2 h. The typical magnitude of this drift is 1-2% and 0.5-1.0% for Mg/Ca and Sr/Ca, respectively, per hour. This drift is mainly attributed to the Gaussian peak characteristic, unstable room temperature, various plasma conditions, and drift in the electronics. In order to correct for these types of variability, a standard solution with a similar matrix was measured for every 4-5 samples. Ratios were corrected off-line using linear interpolation. Short-term external (or between-run) precisions of 0.5% and 0.4% can then be achieved for Mg/Ca and Sr/Ca analyses, respectively (Fig. 1).

3.3. Matrix effects

3.3.1. [Ca] on Mg/Ca and Sr/Ca ratios

A significant interference of [Ca] level on Mg/Ca measurements, with an inverse relationship, is displayed in Fig. 2a. The phenomenon is similar to that observed on ICP-SF-MS (Rosenthal et al., 1999). Mg/Ca ratios varied by 4% over the [Ca] range of 1-10 ppm. The measured Mg/Ca ratio can be corrected using an empirical regression with Mg/Ca_{true}= $-0.018 \times ([Ca]_{standard} - [Ca]_{sample}) +$ Mg/Ca_{measured} (Fig. 2a), This matrix effect is negligible if the [Ca] difference between standard and sample solution is 2 ppm or less. Sr/Ca data are not significantly affected by [Ca] (Fig. 2b), in agreement with the observations in Marchitto (2006). Sr/Ca ratios were constant within the analytical precision over a range of different [Ca] levels of 1-10 pm. The uncertainties of between-run Sr/Ca means are 0.4-0.5% at [Ca] of 6-8 ppm, and better than 0.8-1.7% at [Ca] of 1-5 ppm, due to lower intensities of ion beams. Accordingly,



Fig. 3. (a) Matrix effect of Sr/Ca on Mg/Ca determination with a slope of -0.32% per mmol/mol. This effect causes a bias of less than 0.1% for the measured Mg/Ca ratio in foraminiferal (Sr/Ca: 1.4–1.6 mmol/mol; dark gray area) and coral samples (Sr/Ca: 8.8–9.2 mmol/mol; gray area) (insets). (b) Matrix effect of Mg/Ca on Sr/Ca determination. External variation of measured Sr/Ca data, $\pm 0.17\%$ (2 σ , gray area), is less than the long-term uncertainty of $\pm 0.49\%$, suggesting that there is no significant effect of Mg level on Sr/Ca determination.

[Ca] was prepared to be 7 ppm in the standard and adjusted to the range of 6–8 ppm in the sample solution.

3.3.2. Sr/Ca on Mg/Ca ratio

The Sr/Ca ratio affects the determination of Mg/Ca ratios by a factor of -0.32% per mmol/mol (Fig. 3a). This effect is caused by the formation of ${}^{86}\text{Sr}^{2+}$, which influences the measurement of the ⁴³Ca⁺ ion beam and the accuracy of the Mg/Ca analysis. The ⁸⁶Sr doubly charged ion contributes about 3% and 0.3% of the ⁴³Ca⁺ signal for coral and foraminiferal samples, respectively. Fortunately, the plausible range of Sr levels in the two natural carbonate samples cannot significantly bias the Mg/Ca determination. The amplitudes of glacialinterglacial change and seasonal difference of coral Sr/ Ca ratios are 0.3–0.4 mmol/mol or less (e.g., Guilderson et al., 1994; Shen et al., 1996; Gagan et al., 2000). The variation of foraminiferal Sr/Ca over the last glacial maximum was 0.2 mmol/mol (e.g., Stoll et al., 1999; Shen et al., 2001). This effect, therefore, causes a minimal offset less than 0.1% for determining Mg/Ca in both carbonate samples. For some carbonates with extensive magnitudes of Sr/Ca variation of 2-9 mmol/ mol, such as mollusk shells and otoliths (Bath et al., 2000; Purton et al., 2001), measured Mg/Ca should be corrected using an empirical relationship, Mg/Ca_{true}= $(1-0.32\% \times (Sr/Ca_{standard} - Sr/Ca_{sample})) \times Mg/Ca_{measured}$.

3.3.3. Mg/Ca on Sr/Ca ratio

External variability of measured Sr/Ca data was only 0.17% for the standard with different Mg contents (Fig. 3b). This uncertainty is similar to within-run precision and smaller than the long-term reproducibility (0.49%), suggesting that there is no significant interference of Mg level on Sr/Ca determination.

4. Accuracy, precision and sample size

Uncertainties of Mg/Ca and Sr/Ca ratios in the secondary standards, used for determining elemental ratios in natural samples, are estimated to be ~0.6%, based on the reports given by High-Purity Standards (Charleston, SC). Elemental ratios in these standard solutions were calibrated using primary standard solutions, which were prepared gravimetrically with a precision better than 0.03%. For the Mg/Ca ratio in the secondary standards, a discrepancy of 1.1% was found between the calibrated value and the expected ratio based on High-Purity Standards reports. A discrepancy of only 0.3% was found for the Sr/Ca ratio in the secondary standards.



Fig. 4. Long-term duplicate measurements of (a) Mg/Ca and (b) Sr/Ca ratios in a foraminiferal reference solution, FORAM-GM, over two periods, June–October (Period I, solid circles) and October–December (Period II, open circles) in 2005. The 2σ level and averaged value of Mg/Ca ratios in Period I are 0.32% larger and 1.5% lower than those in Period II, respectively. The external precision of $\pm 0.49\%$ for Sr/Ca in Period II with fresh standard solutions is better than that of $\pm 0.68\%$ in Period I (see text for details).

The short-term external uncertainty is 0.5% for Mg/ Ca and 0.4% for Sr/Ca (Fig. 1). The long-term performance was evaluated using the foraminiferal reference solution, FORAM-GM, over two periods, June–October and October–December, 2005 (Fig. 4). The average Mg/Ca value of 2.513 ± 0.005 (2σ of the mean, $2\sigma_m$) mmol/mol in Period I is 0.037 mmol/mol (1.5%) lower than that of Period II (2.550 ± 0.004 mmol/ mol). These discrepancies could be caused by Mg contamination in the working standard used during Period I. PE bottles were used for the storage of 7-ppm-[Ca] working standard solutions, which were diluted from the concentrated secondary standard solution every two to three months. However, in Period II, the working standard was kept in acid-cleaned Teflon bottles. The FORAM-GM solution was stored in a Teflon bottle over the two periods and was free of Mg contaminant. The low Mg/Ca ratio of the FORAM-GM measured during Period I possibly reflects the positive bias from the contaminated working standard solution (Fig. 4). The 2σ level of the Mg/Ca ratio of ± 0.029 (1.16%) mmol/ mol in Period I is also larger than that of ± 0.021 (0.84%) mmol/mol in Period II. This could be caused by Mg contamination and/or the occasional anomalous behavior of ICP-QMS over the course of several months, as indicated by the clustering of outlying data points (Fig. 4). For Sr/Ca analysis, an external precision of



Fig. 5. Duplicate measurements of one (a) summer and one (b) winter subsample of the Xisha coral. Averages of the ICP-QMS duplicates are shown as dashed lines with long-term between-run uncertainty as dark gray areas, and TIMS data uncertainty as light gray areas. (c) Three duplicate analyses of five 1992 monthly-resolution subsamples of the Nanwan *Porites*, NW940101. Average means are shown with 2σ , all matching TIMS data with precision of $\pm 0.05\%$ (diamonds; Shen et al., 1996).

 $\pm 0.49\%$ in Period II is better than $\pm 0.68\%$ in Period I. If the measurements with contaminated standard in Period I are excluded, the developed ICP-QMS techniques provide a long-term reproducibility of $\pm 0.84\%$ for Mg/ Ca and $\pm 0.49\%$ for Sr/Ca determinations (Fig. 4).

The accuracy of the developed technique can be further verified by comparing ICP-QMS Sr/Ca data to gravimetrically calibrated ID-TIMS measurements with a precision of 0.05% (Shen et al., 1996). For two subsamples of the Xisha coral, ICP-QMS duplicate measurements show no significant difference in comparison with ID-TIMS data (Chiu, 1999; Fig. 5). Results of three replicate Sr/Ca measurements for 3 summer and 2 winter subsamples of *Porites* coral, NW940101, during a 2-month period are shown in Fig. 5c. The between-run precisions range from 0.17–0.54%, illustrating the good reproducibility of this technique. All ICP-QMS data are consistent with TIMS measurements (Fig. 5).

5. Application

Our new technique was applied to coral samples, collected from Xisha Island and Nanwan, and plank-

tonic foraminiferal samples from core MD01-2390, recovered from the southern South China Sea.

Our ICP-QMS method achieved a precision of 0.49% and a corresponding uncertainty of 0.6 °C using coral Sr/Ca thermometry with a sensitivity of 0.8%/°C (Beck



Fig. 6. A three-year (2000–2002) Sr/Ca record of the Nanwan coral *Porites*, NW0310. Coral Sr/Ca-inferred SST data were calculated with an equation given by Shen et al. (1996). In 2002, the inferred SSTs are in agreement with the *in-situ* instrumental data. Note that the coral data are not calendared and simply plotted versus distance (mm) to the top of coral head. Long-term reproducibility of Sr/Ca measurement is shown as black vertical bar.



Fig. 7. Last glacial/interglacial planktonic foraminiferal Mg/Ca record of core MD01-2390 (Steinke et al., 2006).

et al., 1992; Shen et al., 1996; Gagan et al., 2000). Three-year skeletal Sr/Ca records from 2000 to 2002 for a living *Porites* coral head, NW0310, are plotted in Fig. 6. The Sr/Ca ratios ranged from 8.85–8.90 mmol/ mol in summer to 9.06–9.12 mmol/mol in winter. This corresponds to summer and winter SST of 27.5–28.5 °C and 23.5–24.0 °C, respectively, using a coral Sr/Ca-temperature calibration developed by Shen et al. (1996). SST increased from 23.9 °C in early 2002 to 29.2 °C in mid-2002, which matches *in-situ* instrumental observations (Fig. 6).

For foraminiferal Mg/Ca thermometry with a sensitivity of 9%/°C (Elderfield and Ganssen, 2000; Dekens et al., 2002; Anand and Elderfield, 2003), the analytical uncertainty of 0.5% offered by our ICP-QMS method corresponds to 0.1 °C. The precision of this paleothermometer, however, is dominantly constrained by physiology and post-depositional alteration (e.g., Rosenthal and Lohmann, 2002; Steinke et al., 2005). An 882.5 cm-long record of Mg/Ca ratios of the planktonic foraminifera G. ruber from core MD01-2390, covering the last 22,000 years, is shown in Fig. 7 (Steinke et al., 2006). Holocene Mg/Ca values range from 4.2-4.8 mmol/mol, whereas the last glacial section contains values of 3.1-3.5 mmol/mol. The record suggests a glacial-interglacial temperature difference of ~3 °C (Steinke et al., 2006). This finding is consistent with previous studies from the Western Pacific Warm Pool (Lea et al., 2000; Stott et al., 2002; Rosenthal et al., 2003; Visser et al., 2003).

6. Comparison with other techniques

Hot plasma conditions with RF power levels of 1200–1300 W were used in other ICP-MS techniques (e.g., Rosenthal et al., 1999; Yu et al., 2005b). To overcome the high spectral interference inherent to this hot plasma condition, high [Ca] solutions were

introduced and consequently both pulse-counting and analog detection modes had to be used (e.g., Rosenthal et al., 1999; Marchitto, 2006). The inevitable problems of Ca deposition on sampling cones and crosscalibration of two detection modes are introduced by this method. In our new cold plasma method, Ca deposition was remarkably reduced by diluting [Ca] from 100s ppm to 7 ppm. Associated with a dry introduction system, a cold plasma condition was used to decrease the spectral interference. The background counts are less than 0.05% of the signals at m/z=24, 43, and 86 using only pulse-counting mode.

Matrix effects have been known to be more serious for cold plasma conditions than hot plasma conditions (Niu and Houk, 1996; Wollenweber et al., 1999; Murphy et al., 2002). For example, a serious effect of nitric acid on the intensities of ⁷Li,²³Na, ³⁹K, ⁴⁰Ca and ⁵⁶Fe and elemental ratios was found for an ICP-MS, PlasmaQuad II Turbo+, with a 620-W cold plasma condition and a double-pass Scott type chamber

Table 3

Analytical precision and sample size for different techniques of carbonate Mg/Ca and Sr/Ca measurements

Method	Precision (%, 2σ)		Sample size (µg) (selected)	Reference	
	Mg/Ca	Sr/Ca	(selected)		
ID-TIMS		0.05		Beck et al., 1992; Shen et al., 1996	
ID-ICP-QMS		0.5		[#] Le Cornec and Correge, 1997	
ID-ICP-QMS	4	2		[#] Lea et al., 1999	
ID-ICP-QMS	1.34	0.54	100-200	[#] Sun and Sun, 2002	
ICP-QMS	2.8	1.8	60	[#] Yu et al., 2005b	
ICP-SF-MS	0.9	0.9	5-10	Rosenthal et al., 1999	
ICP-SF-MS	1.4			[#] Lea et al., 2003	
ICP-SF-MS	1.1	1.1	10	#Marchitto, 2006	
ICP-AES	1.0	0.4	50	Schrag, 1999	
ICP-AES	0.6	0.6	100-200	de Villiers et al., 2002	
ICP-AES	1.04	0.56		Sun and Sun, 2003	
Cold Plasma ICP-QMS	0.84	0.49	3.5	This study	

Note: [#] Methods were developed for multi-elemental ratios. Precision and sample size may be improved and reduced if only Ca, Mg and Sr are measured.

ID-TIMS: Isotope dilution thermal ionization mass spectrometry.

ID-ICP-QMS: Isotope dilution inductively coupled plasma quadrupole mass spectrometry.

ICP-SF-MS: Inductively coupled plasma sector field mass spectrometry. ICP-AES: Inductively coupled plasma atomic emission spectroscopy. Cold Plasma ICP-QMS: Cold plasma inductively coupled plasma quadrupole mass spectrometry. (Wollenweber et al., 1999). In this study, a dry introduction system of MCN6000 also helped to minimize matrix effects. An interference of [Ca] level on Mg/Ca determination, ~4% per ppm [Ca] (Fig. 2a), is similar to the observed relation on ICP-SF-MS with a hot plasma condition (Rosenthal et al., 1999). A longterm reproducibility and accuracy of 0.4–0.8% is possible using the newly developed method (Figs. 4, 5). The results suggest that the matrix effect in this system has been well corrected and high precision carbonate Mg/Ca and Sr/Ca measurements can be made. This analytical capacity is better than those of previous ICP-QMS methods (Table 3).

A comparison of the analytical precision provided by this ICP-QMS method and other spectrometric techniques is listed in Table 3. TIMS methods give the best precision of 0.05% (e.g., Beck et al., 1992; Shen et al., 1996); however, the labor-intensive aspect of TIMS carries with it the disadvantages of low sample throughput, high cost, and subtle instrument operation. ICP-AES and ICP-SF-MS techniques offer high sample throughput on the order of one sample per 2-5 min, and good analytical precision of 0.4-1.0% for Sr/Ca and 0.6-1.0% for Mg/Ca (Schrag, 1999; Rosenthal et al., 1999; de Villiers et al., 2002; Marchitto, 2006). Our newly developed ICP-QMS method provides simple instrumental operation, high sample throughput on the order of one sample per 5 min, and equally good precision of 0.49% for Sr/Ca and 0.84% for Mg/Ca. Moreover, the use of a 7 ppm [Ca] working solution carries the additional advantage of minimizing sample size requirements down to 3.5 µg, instead of 5–200 µg used in the other spectroscopic techniques (Schrag, 1999; Rosenthal et al., 1999; de Villiers et al., 2002; Sun and Sun, 2003; Marchitto, 2006). This sample size advantage may even allow the investigation of elemental ratios in single foraminiferal tests. Establishment of high resolution and high precision trace metal records in other carbonates, such as mollusks and speleothems, could also be carried out using this technique. Some techniques, developed for measurements of multielements in carbonates, such as Lea et al. (1999) and Yu et al. (2005b), give uncertainties of 1–4% for Sr/Ca and Mg/Ca. The precision and sample size can be improved and reduced by measuring only limited elements and/or using of different introduction systems.

7. Conclusions

In order to develop high precision Mg/Ca and Sr/Ca measurements using ICP-QMS, we have addressed the problems of spectral interferences, instrumental blank,

mass discrimination, and ratio drift. A cold plasma technique with a RF power of 650 W and a desolvation system were used to reduce the spectral background. Mg/ Ca and Sr/Ca ratios were determined directly from intensity ratios with a standard-bracketing method to correct for mass discrimination and ratio drift. The influence of the doubly-charged ion ⁸⁶Sr on the measurement of the ⁴³Ca⁺ ion beam and its influence on measured Mg/Ca ratios were also addressed. Measurements of standards and samples by ICP-QMS and TIMS verify this methodology and demonstrate that this technique can provide a high within-run precision and good long-term external reproducibility for Mg/Ca and Sr/Ca measurements.

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