Contents lists available at ScienceDirect

Journal of Asian Earth Sciences

Determination of element/Ca ratios in foraminifera and corals using cold- and hot-plasma techniques in inductively coupled plasma sector field mass spectrometry

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ARTICLE INFO

ABSTRACT

We have developed a rapid and precise procedure for measuring multiple elements in foraminifera and corals by inductively coupled plasma sector field mass spectrometry (ICP-SF-MS) with both cold- [800 W radio frequency (RF) power] and hot- (1200 W RF power) plasma techniques. Our quality control program includes careful subsampling protocols, contamination-free workbench spaces, and refined plastic-ware cleaning process. Element/Ca ratios are calculated directly from ion beam intensities of ^{24}Mg, ^{27}Al, ^{43}Ca, ^{55}Mn, ^{57}Fe, ^{86}Sr, and ^{138}Ba, using a standard bracketing method. A routine measurement time is 3–5 min per dissolved sample. The matrix effects of nitric acid, and Ca and Sr levels, are carefully quantified and overcome. There is no significant difference between data determined by cold- and hot-plasma methods, but the techniques have different advantages. The cold-plasma technique offers a more stable plasma condition and better reproducibility for ppm-level elements. Long-term 2-sigma relative standard deviations (2-RSD) for repeat measurements of an in-house coral standard are 0.32% for Mg/Ca and 0.43% for Sr/Ca by cold-plasma ICP-SF-MS, and 0.69% for Mg/Ca and 0.51% for Sr/Ca by hot-plasma ICP-SF-MS. The higher sensitivity and enhanced measurement precision of the hot-plasma procedure yields 2-RSD precision for μmol/mol trace elements of 0.60% (Mg/Ca), 9.9% (Al/Ca), 0.68% (Mn/Ca), 2.7% (Fe/Ca), 0.50% (Sr/Ca), and 0.84% (Ba/Ca) for an in-house foraminiferal standard. Our refined ICP-SF-MS technique, which has the advantages of small sample size (2–4 μg carbonate consumed) and fast sample throughput (5–8 samples/hour), should open the way to the production of high precision and high resolution geochemical records for natural carbonate materials.

1. Introduction

Element to calcium (E/Ca) ratios in foraminiferal calcite and coral aragonite have been shown to be related to ambient seawater physical and chemical characteristics through in situ observations (e.g., Shen et al., 1996; Anand et al., 2003), culturing experiments (Nürnberg et al., 1996; Lea et al., 1999; Mashiotta et al., 1999; Russell et al., 2004; Hönisch et al., 2011), and core top calibration approaches (Elderfield and Ganssen, 2000; Lea et al., 2000; Dekens et al., 2002; Rosenthal and Lohmann, 2002). Seawater temperature, for example, can be inferred from foraminiferal Mg/Ca and coral Sr/Ca ratios (e.g., Beck et al., 1992; Guilderson et al., 1994; Nürnberg et al., 1996; Shen et al., 1996; Lea et al., 1999; 2000; Schrag, 1999; Elderfield and Ganssen, 2000; Gagan et al., 2000; Anand et al., 2003; Linsely et al., 2004; Yu et al., 2005b; Steinke et al.,

2006; Linsely et al., 2010). In addition, riverine runoff can be inferred from foraminiferal Ba/Ca (e.g., Hall and Chan, 2004; Weldeab et al., 2007) and Mn/Ca ratios (e.g., Klinkhammer et al., 2009), and upwelling and terrestrial input from coral Ba/Ca ratio (e.g., Lea et al., 1989; McCulloch et al., 2003).

Measurement precision, sample size, and sample throughput are important issues that determine the efficacy of high-resolution carbonate E/Ca methodologies. Isotope dilution thermal ionization mass spectrometry (ID-TIMS) methods (e.g., Beck et al., 1992; Shen et al., 1996; Murphy et al., 2002) offer the best in precision (<0.1%). However, laborious sample preparation procedures, slow sample throughput and high cost limit its broad application. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) methods (e.g., Schrag, 1999; de Villiers et al., 2002; Wara et al., 2003; Andreasen et al., 2006) have the advantage of a large dynamic working range, synchronous detection of multiple elements, and high sample throughput, and can give good precision of 0.4–4% (2 relative standard deviations, 2-RSD) for mmol/mol level

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elements in carbonate minerals. The relatively low sensitivity of ICP-AES instrumentation, however, hinders the precise measurement of μmol/mol level trace elements (e.g., Fig. 4c of Wara et al. (2003)). ICP-quadrupole mass spectrometry (ICP-Q-MS) (e.g., LeCornec and Correge, 1997; Lea et al., 1999; Sun and Sun, 2002; Yu et al., 2005a), with relatively high sensitivity, can provide a 2-RSD of 2–10% for mmol/mol to μmol/mol level elements in carbonate samples as small as 50–100 μg. An external 2-RSD precision of 0.5–0.8% for Mg/Ca and Sr/Ca can be achieved with only 3–10 μg of carbonate when using a desolvation introduction system and carefully addressing interferences and biases (Shen et al., 2007). Due to the Gaussian peak characteristics, the ultimate measurement precision is highly dependent on instrumental stability. Previous studies have shown that the flat-topped peak shape, large dynamic working range and high sensitivity given by ICP-sector field (SF)-MS result in high-precision E/Ca data with a few micrograms carbonate (Rosenthal et al., 1999; Andreasen et al., 2006; Marchitto, 2006).

The high-precision carbonate ICP-SF-MS technique with 2-RSD precision of 0.90% for both Mg/Ca and Sr/Ca was first proposed by Rosenthal et al. (1999) to determine E/Ca ratios with a standard bracketing method for 25 μg carbonate samples. Sample size was reduced to 5–10 μg carbonate in the studies of Andreasen et al. (2006) and Marchitto (2006), which carefully evaluated the effect of Ca concentration ([Ca]) on E/Ca determinations. On the basis of their findings, we addressed more critical factors for ICP-SF-MS work in this study, including: (1) procedure blank, which is very important for carbonate sample less than 10 μg; (2) matrix effects of nitric acid concentration on E/Ca ratios; and (3) interference of doubly-charged $^{86}Sr^{2+}$ ions on determinations of $^{43}Ca^+$ and the Mg/Ca ratio. We also propose different data acquisition protocols with cold- and hot-plasma techniques for measurement of multi-elemental or 1–2 elemental ratios. Furthermore, the sample size required for our refined ICP-SF-MS protocol was reduced to only 2–4 μg of carbonate consumed during the instrumental analysis step and the long-term 2-RSD reproducibility was improved to 0.3–0.7% for Mg/Ca and Sr/Ca. The biogenic carbonates we analyzed include planktonic foraminifera (*Globigerinoides sacculifer* and *Pulleniatina obliquiloculata*) in the Solomon Sea and modern *Porites* corals from the western South China Sea.

2. Experiments

2.1. Labware, standards and samples

All chemical procedures were performed in a metal-free class-10,000 clean room with class-100 working bench at the High-Precision Mass Spectrometry and Environment Change (HISPEC) Laboratory, Department of Geosciences, National Taiwan University. Teflon bottles and beakers for standard preparation were cleaned in acid baths (Shen et al., 2002). Polyethylene (PE) bottles and vials were cleaned by boiling in 3 N RG grade HNO_3 (JT Baker) for 4 h and rinsed with Milli-Q Element water (18.2 Ω) (Shen et al., 2007). However, high background signals of $10-10^4$ counts per second (cps) at low-high masses, such as 24, 27, 43, 55, 57, 86, and 138, were found in PE vials used for sample cleaning, dissolution, and instrumental analysis (Fig. 1). An additional cleaning step was introduced. After cleaning the PE vials with 3 N RG grade HNO_3 using a water-bath method, they were then filled with 5% ultra-pure JT Baker HNO_3 (+0.1% ultra-pure JT Baker HF) and left to leach for at least 3 days. As a result of this extra step, background signals for ^{24}Mg, ^{27}Al, and ^{138}Ba were effectively reduced by 1–2 orders of magnitude comparing with our previous cleaning procedure (Shen et al., 2007).
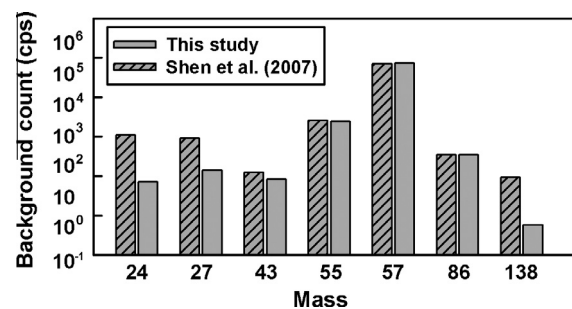

Fig. 1. Spectral background levels with 5% HNO_3 in the PE vials cleaned by methods described in this study (gray bars) and Shen et al. (2007) (slashed bars) on ICP-SF-MS with an RF power of 800 W.

Two primary Mg/Ca and Sr/Ca standard solutions were prepared gravimetrically with high purity metal magnesium chips (99.99%), calcium carbonate powder (≥99.999%), and strontium carbonate powder (99.995%) in Teflon-ware (Shen et al., 2007). Three secondary standard solutions, for determinations of E/Ca ratios in planktonic and benthic foraminifera, and coral samples, were prepared gravimetrically with different mixes of high purity 1000 ± 3 ppm Mg, Ca, Sr and diluted aliquots from 1000 ± 3 ppm Al, Mn, Fe, and Ba (High Purity Standard). Mg/Ca and Sr/Ca ratios in the mixed secondary standards were calibrated with the primary standards. Bracketed standards for routine measurements were prepared by diluting secondary standard solutions.

Foraminiferal and coral standard solutions were also prepared for routine in-run measurements. A batch of 2000 tests of the planktonic foraminifera, *Globorotalia menardii* (>500 μm), from marine sediment core ODP 1115B (9°11′S, 151°34′E; water depth 1149 m) was cleaned in successive steps following the cleaning protocol developed by Shen et al. (2001) and Barker et al. (2003) with a reductive step to avoid contamination from Mn–Fe oxide (Pena et al., 2005). The cleaned foraminiferal tests were dissolved with 5% HNO_3 in a 2-L Teflon bottle as a foraminiferal standard solution FORAM-GM (Shen et al., 2007). A 2-L Teflon bottle of coral standard solution CORAL-M was prepared by dissolving a cleaned 228-g fragment of a modern *Porites* coral collected from Nanwan, southern Taiwan (21°58′N, 120°42′E) in 5% HNO_3. [Ca] in both standards were adjusted to 3 ppm for instrumental measurement runs to evaluate long-term reproducibility. Three powdered *Porites* coral working standards with ID-TIMS Sr/Ca ratios measured at the Australian National University (ANU) were used for accuracy evaluation.

The samples of foraminifera analyzed in this study are from marine core MD05-2925 (9°15′S, 151°34′E, 1642 m water depth) drilled during the Past Equatorial Climate: Tracing El Niño (PEC-TEN) cruise in 2005, supported by the International Marine Past Global Changes Study (IMAGES) program. Twenty-to-thirty planktonic foraminiferal tests of *G. sacculifer* (300–355 μm), and *P. obliquiloculata* (355–425 μm), were picked for analysis at intervals within the uppermost 300-cm section of the core. For the coral analysis, a modern *Porites* colony (ST0506) was collected 1 km offshore of central Vietnam (16°12′N, 108°11′E, 4 m water depth) in the western South China Sea. Foraminiferal and coral samples were treated with the same laboratory procedure used for the foraminiferal and coral standards, and then dissolved in 5% HNO_3 for ICP-SF-MS analysis.

2.2. Instrumentation

Measurements of E/Ca ratios were performed on a Thermo Electron Element II ICP-SF-MS housed at the HISPEC Laboratory, Department of Geosciences, National Taiwan University. The

ICP-SF-MS was operated at low resolution ($M/\Delta M = 300$). Two different radio frequency (RF) power levels were used. The cold-plasma procedure with low RF power of 800 W was chosen to optimize for low background levels, stable plasma conditions, stable ion beam intensities, and high precision elemental ratios. The hot-plasma method with high RF power of 1200 W was used to effectively increase ion beam intensities of low-abundance elements. Sample Ar flow was set at 0.7–0.9 L/min, cooling Ar at 16 L/min, and auxiliary Ar at 0.8–1.0 L/min.

The sample introduction system contains a micro-autosampler device ASX-100 (CETAC Technologies Inc.), a self-aspirating Teflon microconcentric nebulizer ESI-50 µL (ESI Inc.), and a quartz Scott-type double-pass spray chamber. This wet introduction system provides blank levels of 300 cps at mass 24, 1000 cps at mass 43 and 1200 cps at mass 86 for 5% HNO_3 with 1200 W RF power, which are about 2–5 times lower than blank levels obtained with 800 W RF power (Fig. 1). The overall sensitivities were 0.6–1.2 × 10^6 cps for ^{24}Mg (Mg ~ 9 ppb), 1.0–1.2 × 10^6 cps for ^{43}Ca, and 1.0–1.6 × 10^6 cps for ^{86}Sr (Sr ~ 58 ppb) in 3 ppm [Ca] coral and foraminiferal standard solution at an uptake rate of 50 µL/min.

Ion beam intensities were all detected in pulse-counting mode under both 800-W and 1200-W plasma conditions. Measured ion beam intensities of ^{24}Mg, ^{27}Al, ^{43}Ca, ^{55}Mn, ^{57}Fe, ^{86}Sr, and ^{138}Ba were used to determine Mg/Ca, Al/Ca, Mn/Ca, Fe/Ca, Sr/Ca, and Ba/Ca ratios. It is important to point out that ^{46}Ca, with a rare abundance of 0.004% and isobarically influenced by ^{46}Ti, was not selected for determination of Ca levels. The calcium hydride form is 0.01–0.04% (CaH^+/Ca^+) in our system. The interference of $^{42}CaH^+$ on ^{43}Ca is 0.05–0.2%. The natural fractionations of calcium isotopes are less than 1% (Skulan and DePaolo, 1999). This hydride-derived uncertainty on E/Ca ratios is estimated to be only 0.00005–0.002%.

Even before each analysis, the introduction system was flushed with 5% HNO_3 for 70 s to ensure it was clean. Then, a 120-second sample measurement step was performed that included 20-second background signal and 100-second sample signal counts. Each sample was bracketed with a matrix-matched standard (Rosenthal et al., 1999) and only 2–4 µg of carbonate sample was consumed. A sample throughput of 5–8 samples per hour was achieved. All E/Ca ratios were calculated directly from intensity ratios using the external matrix-matched standards. An off-line two-stage data reduction method (Shen et al., 2002) was employed. All errors are given as two standard deviations (2σ) or 2-RSD unless otherwise noted.

Our ICP-SF-MS, equipped with only one secondary electron multiplier (SEM), cannot be used for a simultaneous multi-element analysis. Different data acquisition methods were designed to satisfy different analytical requirements. For example, a short-scan cycle of only 0.14–0.18 s with 2 ion beams (^{43}Ca and ^{86}Sr) or 3 ion beams (e.g., ^{43}Ca, ^{86}Sr, and ^{138}Ba) was designed to obtain high precision measurements of coral Sr/Ca. If multiple elements are of

interest, a long-scan cycle of 0.3–0.4 s, with selected ion beams (e.g., ^{24}Mg, ^{27}Al, ^{43}Ca, ^{55}Mn, ^{57}Fe, ^{86}Sr, and ^{138}Ba), was applied (Table 1).

3. Results and discussion

3.1. Spectral interferences and blanks

Spectral interference is an inevitable issue for any ICP-MS system. The background from polyatomic complexes associated with acids and Ar hinders precise measurements of minor/trace elements, especially for masses less than 80. This interference can be decreased dramatically with low RF power (Wilson et al., 1987; Wollenweber et al., 1999). For example, an interference level at mass 43 decreases from 2000 cps for 1200 W to ~100 cps for 600 W. Cold-plasma techniques with low RF power can also offer a steadier plasma condition and higher measurement precision compared with hot-plasma techniques with RF power >1100 W (Wollenweber et al., 1999; Shen et al., 2007). A cold-plasma condition with 800 W RF power, giving spectral interferences of only 100s, and 600–1000 cps at masses 43 and 86, was selected to determine Sr/Ca ratios at high precision. The cold-plasma procedure is recommended for high-precision coral Sr/Ca thermometry with a thermal sensitivity of only 0.8%/°C (e.g., Beck et al., 1992; Shen et al., 1996; Schrag, 1999; Gagan et al., 2000). A hot-plasma method with 1200 W, offering relatively high sensitivity, was selected to measure low-abundance elements (e.g., Al and Ba). The hot plasma configuration can be used for planktonic foraminiferal Mg/Ca thermometry with a thermal sensitivity of ~9%/°C (e.g., Nürnberg et al., 1996; Lea et al., 1999; Elderfield and Ganssen, 2000; Anand et al., 2003), and also other E/Ca ratios, such as Al/Ca, Mn/Ca, Fe/Ca, and Ba/Ca, during the same run.

Instrumental blanks from the residuum of previously analyzed samples were 10–100s cps, corresponding to 0.01–0.1% for ^{24}Mg, ^{43}Ca and ^{86}Sr. The overall background levels, including polyatomic interference and instrumental blank, range from 0.03% to 1%. This noise was all corrected by the data reduction process.

3.2. Mass discrimination and ratio drift

Mass discrimination, mainly resulting from space charge effects, can limit analytical precision and measurement accuracy (e.g., Rosenthal et al., 1999; Schrag, 1999; Shen et al., 2001, 2007). Low frequency drifting (e.g., Rosenthal et al., 1999; Shen et al., 2007) introduces an error of 0.73% in ^{24}Mg/^{43}Ca and 0.79% in ^{86}Sr/^{43}Ca for a measurement sequence example shown in Fig. 2. In order to overcome this problem, a standard bracketing method and drift correction was applied to the measurement sequence using an off-line linear interpolation calculation (Shen

Table 1
Instrumental settings and data acquisition.

| Isotope	Mass window	Settling time, s	Sample time, s	Samples per peak	Search window	Integration window	Detection mode
Cold plasma mode: low resolution, 1 run × 240 passes							
^{43}Ca	5	0.1	0.05	1	150	80	Counting
^{86}Sr	5	0.04	0.05	1	150	80	Counting
^{138}Ba	5	0.04	0.05	1	150	80	Counting
Hot plasma mode: low resolution, 1 run × 200 passes							
^{24}Mg	5	0.1	0.03	1	150	80	Counting
^{27}Al	5	0.001	0.08	1	150	80	Counting
^{43}Ca	5	0.04	0.03	1	150	80	Counting
^{55}Mn	5	0.026	0.04	1	150	80	Counting
^{57}Fe	5	0.001	0.02	1	150	80	Counting
^{86}Sr	5	0.03	0.03	1	150	80	Counting
^{138}Ba	5	0.03	0.05	1	150	80	Counting
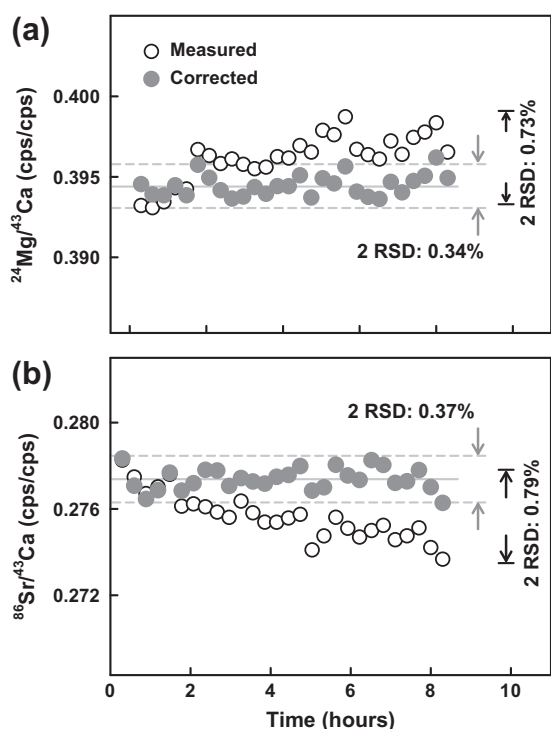
Fig. 2. An example of measured intensity ratio drift in (a) $^{24}Mg/^{43}Ca$ and (b) $^{86}Sr/^{43}Ca$ during an 8-hr experiment (open circles) by hot-plasma techniques. The drift-magnitude of 0.7–0.8% can be corrected to 0.3–0.4% by a standard-bracketing method (grey circles).

et al., 2007). The improved short-term 2-RSD is 0.34% for $^{24}Mg/^{43}Ca$ and 0.37% for $^{86}Sr/^{43}Ca$ (Fig. 2).

3.3. Matrix effects

3.3.1. Acid effect

Ion beam intensities are affected by acid concentration (Wollenweber et al., 1999; Shen et al., 2011). The effect of acid concentration on carbonate E/Ca ratio determinations was reported to

be negligible for ICP-Q-MS with a desolvation introduction system (Shen et al., 2007). However, this effect has not been addressed in the development of ICP-SF-MS techniques with a wet introduction system. Measurements of E/Ca ratios in foraminiferal and coral standard solution aliquots dissolved in 1–6% HNO_3 show a significant acid effect. The example case given in Fig. 3 is for a 3-ppm coral standard, CORAL-M. All ion beam intensity ratios vary significantly across the HNO_3 concentration range of 1–3%, and slightly for 4–6% HNO_3 (Fig. 3). For example, $^{24}Mg/^{43}Ca$ ratios decrease by ~10% and $^{86}Sr/^{43}Ca$ increases by ~8% across the whole range of acid concentrations (Fig. 3a and e). An exponential-like decrease in the ratios is expressed for Al/Ca and Mn/Ca (Fig. 3b and c), whereas there is an opposite increasing trend for Fe/Ca and Ba/Ca (Fig. 3d and f). The result shows a clear acid effect for wet introduction systems and demonstrates that acid concentration must be well titrated to avoid significant biases in E/Ca ratios. A nitric acid concentration of $5.0 \pm 0.1\%$ (2σ) was carefully titrated with dehydrated solid sodium carbonate, instead of sodium hydroxide solution, resulting in <0.1% offset for all E/Ca ratios of interest.

3.3.2. Influence of [Ca] on Mg/Ca and Sr/Ca

A significant influence of [Ca] on carbonate E/Ca ratios has been reported (e.g., Rosenthal et al., 1999). We evaluated the [Ca] effect on Mg/Ca and Sr/Ca ratios by analyzing secondary standard solution CORAL-M diluted over a [Ca] range of 0.5–5 ppm (Fig. 4a). The result shows a 2.5% change in Mg/Ca ratio over the entire [Ca] range, but there is no significant [Ca] effect on Sr/Ca (Fig. 4b). For routine measurements, [Ca] in both sample and standard solutions were adjusted to 3 ppm with a difference <10% to eliminate this effect. The measured Mg/Ca ratio can also be corrected using an empirical regression with $Mg/Ca_{corrected} = -0.019 \times ([Ca]_{standard} - [Ca]_{sample}) + Mg/Ca_{measured}$.

3.3.3. Influence of [Mg] on Sr/Ca and [Sr] on Mg/Ca

Matrix-matched benthic foraminiferal standard solutions with different Mg concentrations and a constant Sr/Ca ratio were used to evaluate the [Mg] effect on Sr/Ca analysis. The external 2-RSD variability of measured Sr/Ca data for four standard solutions with Mg/Ca ratios from 4.1 to 10.3 mmol/mol is only 0.3%, comparable
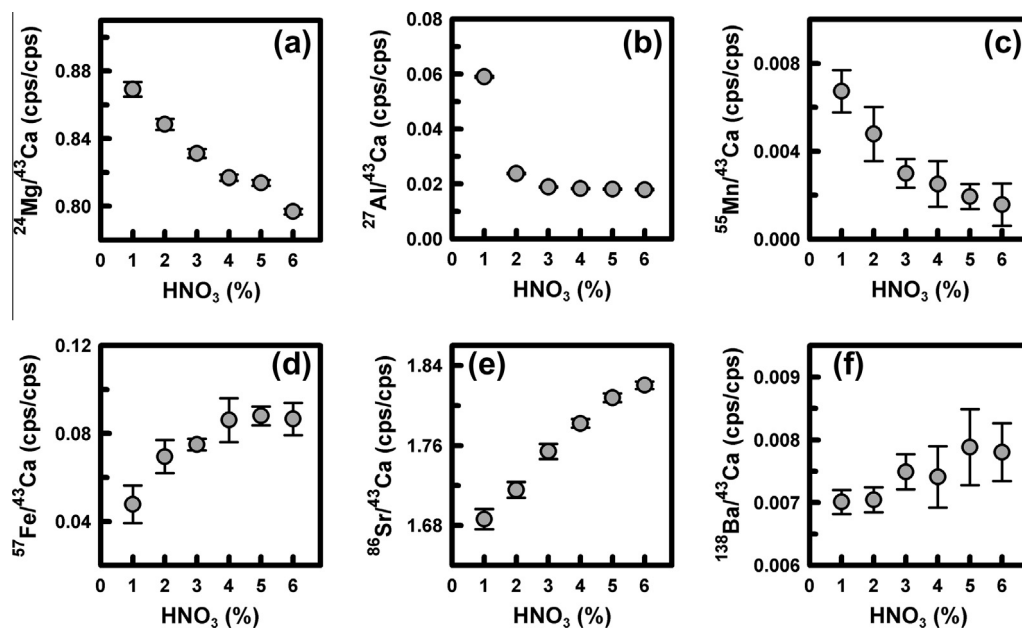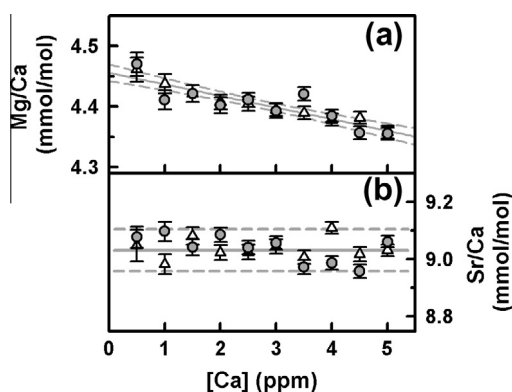

Fig. 3. Matrix effect of nitric acid (1–6%) on (a) $^{24}Mg/^{43}Ca$, (b) $^{27}Al/^{43}Ca$, (c) $^{55}Mn/^{43}Ca$, (d) $^{57}Fe/^{43}Ca$, (e) $^{86}Sr/^{43}Ca$, and (f) $^{138}Ba/^{43}Ca$ intensity ratios with 2-sigma internal error in 3-ppm CORAL-M standard solution measured by hot-plasma ICP-SF-MS.

Fig. 4. Matrix effect of [Ca] on (a) Mg/Ca and (b) Sr/Ca measurements of CORAL-M standard solution by cold-plasma ICP-SF-MS. The influence of [Ca] is significant for Mg/Ca by a factor of $-0.019 \times$ Mg/Ca (mmol/mol)/[Ca] (ppm), but negligible for Sr/Ca. The gray dashed lines denote the 2σ range.
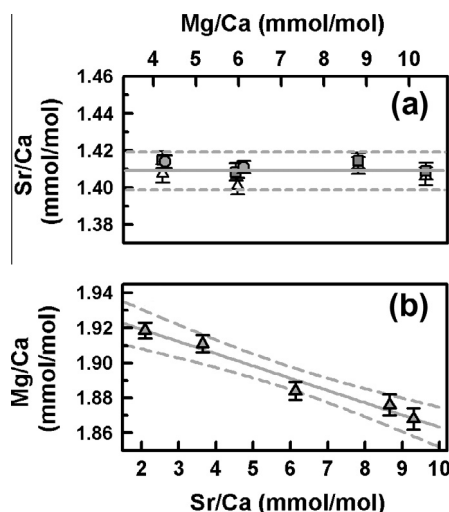

Fig. 5. (a) Matrix effect of [Mg] on Sr/Ca measurements. Three duplicate measurements of four aliquots show no significant change in the Sr/Ca ratios with different Mg/Ca. (b) A matrix effect of [Sr] on Mg/Ca with a slope of -0.36% per mmol/mol Sr/Ca. The solid gray and dashed gray lines represent the average and 2σ ranges.

to the internal precision. Therefore, [Mg] does not produce an observable interference on Sr/Ca analysis (Fig. 5a).

Matrix-matched benthic foraminiferal standard solutions with a constant Mg/Ca ratio and different Sr contents were used to evaluate the effect of [Sr] on Mg/Ca determinations. The Mg/Ca ratio decreases from 1.92 to 1.87 mmol/mol with a Sr/Ca range from 2.1 to 9.3 mmol/mol (Fig. 5b). This decreasing factor of -0.36% per mmol/mol Sr/Ca is probably due to the formation of doubly charged $^{86}Sr^{2+}$ ions (Pupyshev and Semenova, 2001), which biases the measurement of $^{43}Ca^+$. This effect can only cause an Mg/Ca offset of less than 0.1% for environmental signals like the seasonal difference in corals and glacial–interglacial changes in foraminifera (Andreasen et al., 2006; Shen et al., 2007). For natural carbonate samples with extensive Sr/Ca ranges, the measured Mg/Ca should be corrected using the empirical relationship of Shen et al. (2007).

3.4. Precision, reproducibility and accuracy

Two-year replicate Mg/Ca and Sr/Ca measurements of a coral standard solution, CORAL-M, are illustrated in Fig. 6. The internal 2-RSD precision of single runs is 0.1–0.2%. Long-term external precision, the assessment of the data quality, is 0.32% for Mg/Ca and
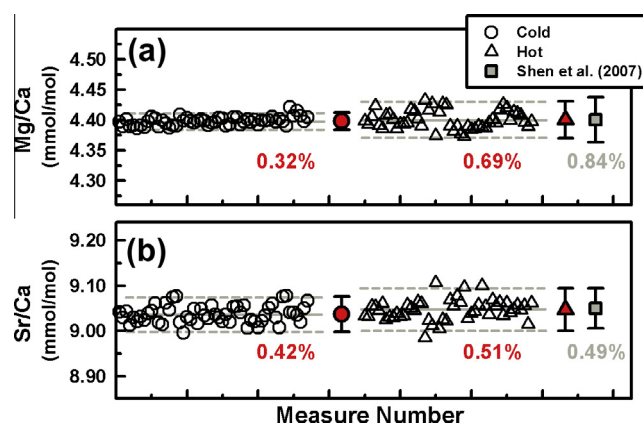
Fig. 6. Two-year reproducibility of (a) Mg/Ca and (b) Sr/Ca measurements (open symbols) for a CORAL-M standard solution by cold- (circles) and hot-plasma (triangles) techniques. The long-term average values (red symbols with 2-sigma error bars) show no significant difference from ICP-Q-MS data (gray square) (Shen et al., 2007). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.42% for Sr/Ca with cold-plasma techniques, and 0.69% for Mg/Ca and 0.51% for Sr/Ca with hot-plasma techniques. These 2-sigma precisions correspond to 0.06 °C for the foraminiferal Mg/Ca thermometer (e.g., Elderfield and Ganssen, 2000; Dekens et al., 2002; Anand et al., 2003) and 0.6 °C for the coral Sr/Ca thermometer. (e.g., Beck et al., 1992; Shen et al., 1996).

The 2-RSD precision yielded by the hot-plasma method is 0.60% (Mg/Ca), 9.9% (Al/Ca), 0.68% (Mn/Ca), 2.7% (Fe/Ca), 0.50% (Sr/Ca), and 0.84% (Ba/Ca) for replicate measurements of our planktonic foraminifer standard FORAM-GM (Fig. 7). To further evaluate compatibility between cold- and hot-plasma methods, 8-year average (1982–1989 AD) Sr/Ca and Ba/Ca ratios of modern coral ST0506 were measured (Fig. 8). The differences between the cold- and hot-plasma datasets are -0.01 ± 0.09 mmol/mol for Sr/Ca and 0.05 ± 0.81 μmol/mol for Ba/Ca. The result demonstrates the good agreement between the two procedures.

Measurement accuracy was evaluated by comparing ICP-SF-MS Mg/Ca and Sr/Ca data to previously developed ICP-Q-MS measurements (Shen et al., 2007), which were verified with gravimetrically calibrated ID-TIMS (Shen et al., 1996). For our coral standard, CORAL-M, the long-term averages of Mg/Ca [4.38 ± 0.01 (cold) and 4.38 ± 0.03 (hot) mmol/mol] and Sr/Ca [9.04 ± 0.04 (cold) and 9.05 ± 0.05 (hot) mmol/mol] agree within error with ICP-Q-MS values (Mg/Ca = 4.38 ± 0.04 and Sr/Ca = 9.04 ± 0.04 mmol/mol, Shen et al., 2007). The means of four duplicate ICP-SF-MS measurements of three ANU coral working standards show no significant difference from ID-TIMS data (Gagan et al., 1998) (Fig. 9). For the planktonic foraminiferal standard, FORAM-GM, the measured values for Mg/Ca (2.55 ± 0.02 mmol/mol) and Sr/Ca (1.33 ± 0.01 mmol/mol) by hot-plasma methods (Fig. 7) match the respective ICP-Q-MS values (Shen et al., 2007). The fidelity of our methodology is also verified by inter-laboratory agreement for planktonic foraminiferal samples and standard solutions by HISPEC and the Department of Geology and Geophysics, Woods Hole Oceanographic Institution (Chen et al., 2010).

3.5. Comparison with previous ICP-SF-MS techniques

Our refined methods offer several advantages compared to previous ICP-SF-MS techniques (Rosenthal et al., 1999; Andreasen et al., 2006; Marchitto, 2006). For example, the [Ca] requirement in dissolved sample solutions was reduced from 10s–100s ppm to only 3–6 ppm in our procedures to eliminate the problem of
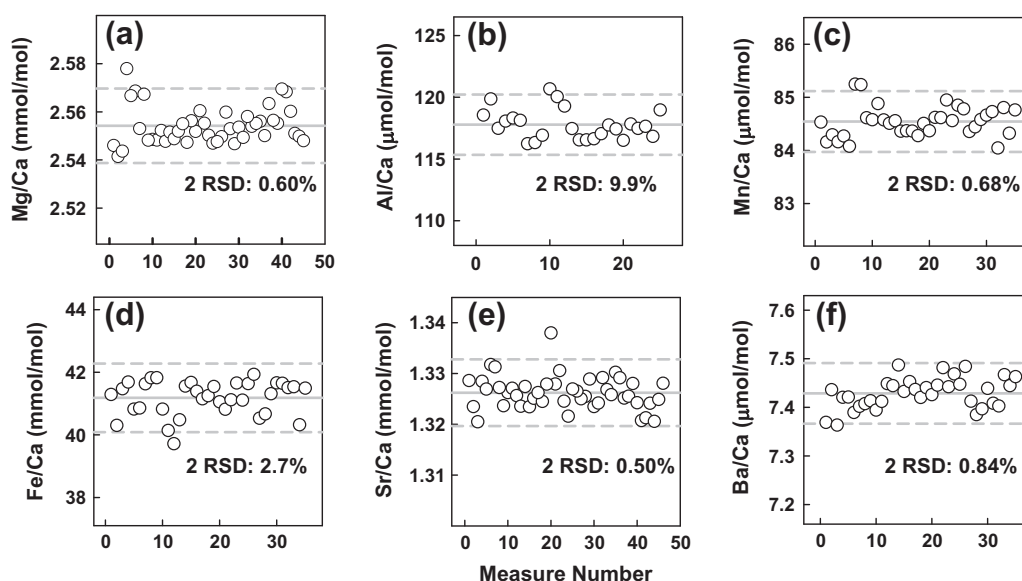
Fig. 7. Short-term reproducibility of (a) Mg/Ca, (b) Al/Ca, (c) Mn/Ca, (d) Fe/Ca, (e) Sr/Ca, and (f) Ba/Ca measurements for an in-house planktonic foraminiferal standard (FORAM-GM). Gray lines are averages and dashed lines represent 2-sigma ranges.
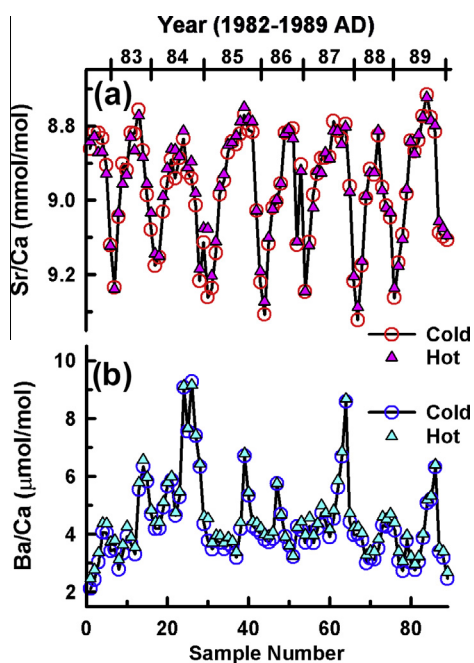

Fig. 8. Comparison of cold-plasma (open circles) and hot-plasma (solid triangles) techniques by determining eight-year-long (1982–1989 AD) monthly-resolved (a) Sr/Ca and (b) Ba/Ca records for *Porites* coral ST0506.

Fig. 9. Four duplicate Sr/Ca measurements (open circles) for three ANU in-house coral standards. The means (solid circles) match ID-TIMS data (squares).

Ca deposition on the interface cones. With this low [Ca] level, pulse-counting mode can be used to measure all ion beam intensities of interest, which were less than 1.5×10^6 cps. Furthermore, cross-calibration between analog and pulse-counting mode was not required. The magnet settling time for the lowest mass was tested and set at 0.10 s, instead of the default value of 0.25–0.30 s. The data acquisition was set at 1 sample per peak, instead of 200 samples per peak used in the previous techniques (Rosenthal et al., 1999; Marchitto, 2006). Scan cycles were shortened from 0.4–0.8 s to only 0.3–0.4 s (Table 1). A serious effect of nitric acid concentration, which was not addressed in the previous studies, was effectively diminished by a careful titration program.
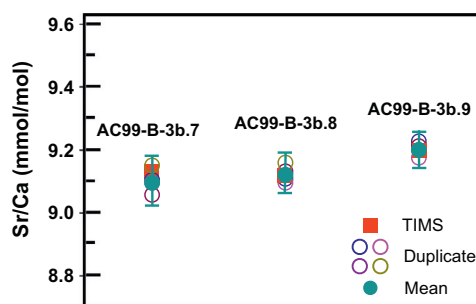
Our protocols, therefore, provide higher internal precision of 0.1–0.2% and 2-RSD reproducibility of 0.3–0.5% for Mg/Ca and Sr/Ca with only 2–4 μg of carbonate consumed.

3.6. Example case studies

Mg/Ca records for two species of planktonic foraminifera (*G. sacculifer* and *P. obliquiloculata*) from core MD05-2925 from the Solomon Sea are plotted over the past 25 kyr BP in Fig. 10. The mean Mg/Ca ratios increase from glacial values of 3.2 mmol/mol to Holocene values of 4.1 mmol/mol for *G. sacculifer* and from 2.3 mmol/mol to 2.8 mmol/mol for *P. obliquiloculata* (Fig. 10). Using a multi-species composite Mg/Ca-sea surface temperature (SST) relationship given by Anand et al. (2003), the corresponding glacial–interglacial temperature changes from 24.8 °C to 28.1 °C for surface seawater and from 20.5 °C to 25.1 °C for upper thermocline seawater. Comparison with planktonic foraminiferal Mg/Ca-seawater temperatures inferred from analysis of marine core MD01-2378 in the Timor Sea (13°5′S, 121°47′E; water depth: 1783 m) (Xu et al., 2008) suggests a relatively stable thermal gradient in the Solomon Sea compared to that in the Timor Sea over the last deglaciation.

A five-year (2000–2004 AD) monthly-resolution Sr/Ca record for a modern *Porites* coral (ST0506) off central Vietnam in the western South China Sea (Shen et al., 2008) is shown in Fig. 11. The
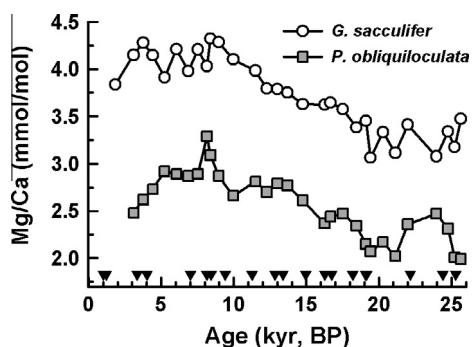
Fig. 10. Solomon Sea surface temperature (open circles) and upper thermocline temperature (gray squares) records over the past 25 kyr inferred from analysis of foraminiferal Mg/Ca in *G. sacculifer* and *P. obliquiloculata* by hot-plasma ICP-SF-MS. Reverse triangles are calibrated accelerator mass spectrometry (AMS) radiocarbon dates.
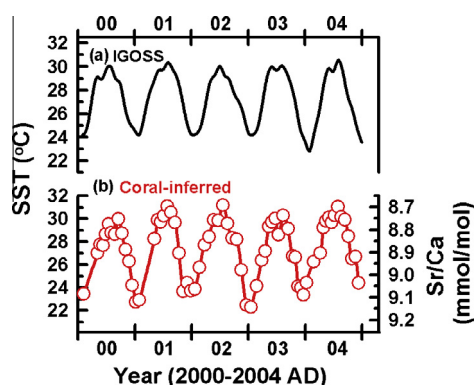
Fig. 11. Comparison of five-year (2000–2004 AD) (a) IGOSS (http://iridl.ldeo.colum-bia.edu/SOURCES/.IGOSS/) satellite-derived and (b) coral Sr/Ca-inferred SST records for the western South China Sea.

seasonal coral Sr/Ca values range from 8.68 to 9.15 mmol/mol. The equivalent SSTs are 23 °C in winter and 30 °C in summer using a coral Sr/Ca-SST calibration established by Shen et al. (1996). The result is in good agreement with regional $1° \times 1°$ satellite (Inte-grated Global Ocean Services System, IGOSS) SST data (Fig. 11a). A 1–2 °C discrepancy between the coral-inferred and IGOSS SST re-cords for two winters (2002–2003, 2003–2004) is probably due to differences in local and regional thermal conditions (Fig. 11b).

4. Conclusions

In order to develop high-precision measurements of foraminif-eral and coral E/Ca ratios by ICP-SF-MS with cold- and hot-plasma conditions, we carefully addressed analytical issues including chemistry, spectral interferences, ratio drifting, and matrix effects. In addition to the effects of [Ca] and Sr/Ca on Mg/Ca analysis, we found a serious nitric acid effect. The nitric acid concentration, used for preparation of dissolved samples and standards, can be carefully titrated to $5.0 \pm 0.1\%$ (2σ) to overcome this influence. Our refined high-sensitivity technique produces good measure-ment reproducibility (2-RSD of 0.3–0.7% for Mg/Ca and 0.4–0.5% for Sr/Ca) and provides high throughput (5–8 samples/hour) with only 2–4 µg of carbonate consumed during the analytical step. Measurements of standards and samples by previous ICP-Q-MS and TIMS support the fidelity of our methods, which can be applied to the determination of trace elements in corals, foraminifera, and other natural carbonates.

References

Anand, P., Elderfield, H., Conte, M.H., 2003. Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series. Paleoceanography. http://dx.doi.org/10.1029/2002PA000846.

Andreasen, D.H., Sosdian, S., Perron-Cashman, S., Lear, C.H., de Garidel-Thoron, T., Field, P., Rosenthal, Y., 2006. Fidelity of radially viewed ICP-OES and magnetic-sector ICP-MS measurement of Mg/Ca and Sr/Ca ratios in marine biogenic carbonate: are they trustworthy together? Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2005GC001124.

Barker, S., Greaves, M., Elderfield, H., 2003. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2003GC000559.

Beck, J.W., Edwards, R.L., Ito, E., Taylor, F.W., Recy, J., Rougerie, F., Joannot, P., Henin, C., 1992. Sea-surface temperature from coral skeletal strontium/calcium ratios. Science 257, 644–647.

Chen, M.-T., Lin, X.P., Chang, Y.-P., Chen, Y.-C., Lo, L., Shen, C.-C., Yokoyama, Y., Oppo, D.W., Thompson, W.G., Zhang, R., 2010. Dynamic millennial-scale climate changes in the northwestern Pacific over the past 40,000 years. Geophys. Res. Lett. http://dx.doi.org/10.1029/2010GL045202.

de Villiers, S., Greaves, M., Elderfield, H., 2002. An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2001GC000169.

Dekens, P.S., Lea, D.W., Pak, D.K., Spero, H.J., 2002. Core top calibration of Mg/Ca in tropical foraminifera: refining paleotemperature estimation. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2001GC000200.

Elderfield, H., Ganssen, G., 2000. Past temperature and δ^{18}O of surface ocean waters inferred from foraminiferal Mg/Ca ratios. Nature 405, 442–445.

Gagan, M.K., Ayliffe, L.K., Hopley, D., Cali, J.A., Mortimer, G.E., Chappell, J., McCulloch, M.T., Head, M.J., 1998. Temperature and surface-ocean water balance of the mid-Holocene tropical western Pacific. Science 279, 1014–1018.

Gagan, M.K., Ayliffe, L.K., Beck, J.W., Cole, J.E., Druffel, E.R.M., Dunbar, R.B., Schrag, D.P., 2000. New views of tropical paleoclimates from corals. Quatern. Sci. Rev. 19, 45–64.

Guilderson, T.P., Fairbanks, R.G., Rubenstone, J.L., 1994. Tropical temperature variations since 20,000 years ago – modulation interhemispheric climate change. Science 263, 663–665.

Hall, J.M., Chan, L.-H., 2004. Ba/Ca in *Neogloboquadrina pachyderma* as an indicator of deglacial meltwater discharge into the western Arctic Ocean. Paleoceanography. http://dx.doi.org/10.1029/2003PA000910.

Hönisch, B., Allen, K.A., Russell, A.D., Eggins, S.M., Bijma, J., Spero, H.J., Lea, D.W., Yu, J., 2011. Planktic foraminifers as recorders of seawater Ba/Ca. Mar. Micropaleontol. 79, 52–57.

Klinkhammer, G.P., Mix, A.C., Haley, B.A., 2009. Increased dissolved terrestrial input to the coastal ocean during the last deglaciation. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2008GC002219.

Lea, D.W., Shen, G.T., Boyle, E.A., 1989. Coralline barium records temporal variability in equatorial Pacific upwelling. Nature 340, 373–376.

Lea, D.W., Mashiotta, T.A., Spero, H.J., 1999. Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. Geochim. Cosmochim. Acta 63, 2369–2379.

Lea, D.W., Pak, D.K., Spero, H.J., 2000. Climate impact of late quaternary equatorial Pacific sea surface temperature variations. Science 289, 1719–1724.

LeCornec, F., Correge, T., 1997. Determination of uranium to calcium and strontium to calcium ratios in corals by inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. 12, 969–973.

Linsely, B.K., Wellington, G.M., Schrag, D.P., Ren, L., Salinger, M.J., Tudhope, Q.W., 2004. Geochemical evidence from corals for changes in the amplitude and spatial pattern of South Pacific interdecadal climate over the last 300 years. Clim. Dyn. 22, 1–11.

Linsely, B.K., Rosenthal, Y., Oppo, D.W., 2010. Holocene evolution and the western Pacific warm pool. Nat. Geosci. 3, 578–583.

Marchitto, T.M., 2006. Precise multielemental ratios in small foraminiferal samples determined by sector field ICP-MS. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2005GC001018.

Mashiotta, T.A., Lea, D.W., Spero, H.J., 1999. Glacial–interglacial changes in Subantarctic sea surface temperature and delta O-18-water using foraminiferal Mg. Earth Planet. Sci. Lett. 170, 417–432.

McCulloch, M., Fallon, S., Wyndham, T., Hendy, E., Lough, J., Barnes, D., 2003. Coral record of increased sediment flux to the inner Great Barrier Reef since European settlement. Nature 421, 727–730.

Murphy, K.E., Long, S.E., Rearick, M.S., Ertas, O.S., 2002. The accurate determination of potassium and calcium using isotope dilution inductively coupled "cold" plasma mass spectrometry. J. Anal. At. Spectrom. 17, 469–477.

Nürnberg, D., Bijma, J., Hemleben, C., 1996. Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. Geochim. Cosmochim. Acta 60, 803–814.

Pena, L.D., Calvo, E., Calvo, I., Eggins, S., Pelejero, C., 2005. Identification and removal of Mn–Mg-rich contaminant phases on foraminiferal test: Implications for Mg/Ca past temperature reconstruction. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2005GC000930.

Pupyshev, A.A., Semenova, E.V., 2001. Formation of doubly charged atomic ions in the inductively coupled plasma. Spectrochim. Acta Part B 56, 2397–2418.

Rosenthal, Y., Lohmann, G.P., 2002. Accurate estimation of sea surface temperatures using dissolution-corrected calibrations for Mg/Ca paleothermometry. Paleoceanography. http://dx.doi.org/10.1029/2001PA000749.

Rosenthal, Y., Field, M.P., Sherrell, R.M., 1999. Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry. Anal. Chem. 71, 3248–3253.

Russell, A.D., Hönisch, B., Spero, H.J., Lea, D.W., 2004. Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera. Geochim. Cosmochim. Acta 68, 4347–4361.

Schrag, D.P., 1999. Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. Paleoceanography. http://dx.doi.org/10.1029/1998PA900025.

Shen, C.-C., Lee, T., Chen, C.-Y., Wang, C.-H., Dai, C.-F., Li, L.-A., 1996. The calibration of D[Sr/Ca] versus sea surface temperature relationship for *Porites* corals. Geochim. Cosmochim. Acta 60, 3849–3858.

Shen, C.-C., Hastings, D.W., Lee, T., Chiu, C.-C., Lee, M.-Y., Wei, K.-Y., Edwards, R.L., 2001. High precision glacial–interglacial benthic foraminiferal Sr/Ca records from the eastern equatorial Atlantic Ocean and Caribbean Sea. Earth Planet. Sci. Lett. 190, 197–209.

Shen, C.-C., Edwards, R.L., Cheng, H., Dorale, J.A., Thomas, R.B., Moran, S.B., Weinstein, S.E., Edmonds, H.N., 2002. Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. Chem. Geol. 185, 165–178.

Shen, C.-C., Chiu, H.-Y., Chiang, H.-W., Chu, M.-F., Wei, K.-Y., Steinke, S., Chen, M.-T., Lin, Y.-S., Lo, L., 2007. High precision measurements of Mg/Ca and Sr/Ca ratios in carbonates by cold plasma inductively coupled plasma quadrupole mass spectrometry. Chem. Geol. 236, 339–349.

Shen, C.-C., Li, K.-S., Sieh, K., Natawidjaja, D., Cheng, H., Wang, X., Edwards, R.L., Lam, D.D., Hsieh, Y.-T., Fan, T.-Y., Meltzner, A.J., Taylor, F.W., Quinn, T.-M., Chiang, H.-W., Kilbourne, K.H., 2008. Variation of initial ^{230}Th/^{232}Th and limits of high precision U–Th dating of shallow-water. Geochim. Cosmochim. Acta 72, 4201–4223.

Shen, C.-C., Wu, C.-C., Liu, Y., Yu, J., Chang, C.-C., Lam, D.D., Chou, C.-J., Lo, L., Wei, K.-Y., 2011. Measurements of natural carbonate rare earth elements in femtogram quantities by inductive coupled plasma sector field mass spectrometry. Anal. Chem. 83, 6842–6848.

Skulan, J., DePaolo, D.J., 1999. Calcium isotope fractionation between soft and mineralized tissues as a monitor of calcium use in vertebrates. Proc. Natl. Acad. Sci. USA 96, 13709–13713.

Steinke, S., Chiu, H.-Y., Yu, P.-S., Shen, C.-C., Erlenkeuser, H., Löwemark, L., Chen, M.-T., 2006. On the influence of sea level and monsoon climate on the southern South China Sea freshwater budget over the last 22,000 years. Quatern. Sci. Rev. 25, 1475–1488.

Sun, Y.-L., Sun, M., 2002. Simultaneous determination of major, minor and trace elements in biocarbonates by inductively coupled plasma mass spectrometry. Anal. Bioanal. Chem. 374, 1338–1340.

Wara, M.W., Anderson, L.D., Schellenberg, S.A., Franks, R., Ravelo, A.C., Delaney, M.L., 2003. Application of a radially viewed inductively coupled plasma-optical emission spectrophotometer to simultaneous measurement of Mg/Ca, Sr/Ca, and Mn/Ca ratios in marine biogenic carbonates. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2003GC000525.

Weldeab, S., Lea, D.W., Schneider, R.R., Andersen, N., 2007. 155,000 years of west African monsoon and ocean thermal evolution. Science 316, 1303–1307.

Wilson, D.A., Vickers, G.H., Hieftje, G.M., 1987. Spectral and physical interferences in a new, flexible inductively coupled plasma mass-spectrometry instrument. J. Anal. At. Spectrom. 2, 365–368.

Wollenweber, D., Strassburg, S., Wunsch, G., 1999. Determination of Li, Na, Mg, K, Ca and Fe with ICP-MS using cold plasma conditions. Fresenius J. Anal. Chem. 364, 433–437.

Xu, J., Holbourn, A., Kuhnt, W.G., Jian, Z.-M., Kawamura, H., 2008. Changes in the thermocline structure of the Indonesian outflow during Terminations I and II. Earth Planet. Sci. Lett. 273, 152–162.

Yu, J., Day, J., Greaves, M., Elderfield, H., 2005a. Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS. Geochem. Geophys. Geosyst. http://dx.doi.org/10.1029/2005GC000964.

Yu, K.-F., Zhao, J.-X., Wei, G.-J., Cheng, X.-R., Wang, P.-X., 2005b. Mid-late Holocene monsoon climate retrieved from seasonal Sr/Ca and δ^{18}O records of *Porites lutea* corals at Leizhou Peninsula, northern coast of South China Sea. Global Planet. Change 47, 301–316.