Direct measurement of ^{44}Ca/^{40}Ca ratios by MC–ICP–MS using the cool plasma technique

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Abstract

Here, we present a new technique for the direct measurement of ^{44}Ca/^{40}Ca isotope ratios on a Multicollector Inductively Coupled Plasma Mass Spectrometer (MC–ICP–MS, AXIOM) using the "cool plasma" technique. By reducing the plasma energy to about 400 W, the isobaric effect resulting from ^{40}Ar^{+} can be significantly reduced, enabling the simultaneous and precise measurement of ^{44}Ca and ^{40}Ca beam intensities in different Faraday cups. In contrast to the TIMS technique requiring a ^{43}Ca/^{48}Ca double spike, the isotope measurements on MC–ICP–MS can be performed by bracketing standards. We express the calcium isotope variation relative to NIST SRM 915a ($\delta^{44/40}$Ca [‰]=[((^{44}Ca/^{40}Ca)$_{sample}$/(^{44}Ca/^{40}Ca)$_{NIST\ SRM\ 915a}$) − 1]*1000). Isobaric effects of ^{24}Mg^{16}O^{+} and ^{23}Na^{16}OH^{+} interfering with ^{40}Ca and ^{26}Mg^{16}OH$_2^{+}$ with ^{44}Ca can be neglected by measuring calcium isotopes near the low-mass edge of the peaks. No influence of ^{87}Sr^{2+} monitored on 43.5 atomic mass units (amu) was found. Repeated measurements of two Johnson Matthey CaCO$_3$ standards (lot No. 4064 and lot No. 9912) revealed values of about − 11.29 (‰ SRM 915a) and 0.57 (‰ SRM 915a). These values are in accordance with previous values published by Russell et al. [Geochim. Cosmochim. Acta 42 (1978) 1075], Heuser et al. [Int. J. Mass Spectrom. 220 (2002) 385], Hippler et al. [Geostand. Newsl. 27 (2003) 267] and Schmitt et al. [Geochim. Cosmochim. Acta 67 (2003) 2607]. Repeated measurement of the NIST SRM 915a CaCO$_3$ standard showed that the variance of a single $\delta^{44/40}$Ca measurement is about 0.14‰ RSD being comparable with TIMS. MC–ICP–MS-based $\delta^{44/40}$Ca values measured on inorganically precipitated aragonite samples are indistinguishable from earlier measurements based on TIMS, confirming the positive correlation of $\delta^{44/40}$Ca and temperature. MC–ICP–MS-based $\delta^{44/40}$Ca measurements on cultured *Orbulina universa* showed a slope of about 0.026‰/°C being similar to the TIMS-based $\delta^{44/40}$Ca measurements showing a slope of about 0.019‰/°C. The large offset of about 5‰ between the two techniques is shown to be caused by a "matrix" effect, indicating that any $\delta^{44/40}$Ca measurements on MC–ICP–MS are sensitively controlled by the Ca concentration and the acidity of the solution. Our study demonstrates the possibility to measure the whole dispersion of calcium isotopes with MC–ICP–MS, showing that ^{40}Ca can be used for normalization of ^{44}Ca.
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1. Introduction

Only few data sets link sea water concentrations of calcium (Ca) or calcium isotope ratios to Earth's biological evolution (Schmitt et al., 2003a,b; De La Rocha and DePaolo, 2000; Arp et al., 2001; Wallmann, 2001; Stanley and Hardie, 1998; Degens, 1979) although Ca plays a major role in biological processes due to its chemical versatility related to its highly adaptable coordination geometry, its divalent charge, modest binding energies, fast reaction kinetics and its inertness in redox reactions (Williams, 1974, 1989). The present lack of data is due to the fact that thermal ionization measurements of Ca are difficult because it is a low-mass element with a relatively large mass dispersion of its isotopes.

Ca has six naturally occurring stable isotopes with atomic mass units (amu) and abundances of: ^{40}Ca (96.941%), ^{42}Ca (0.647%), ^{43}Ca (0.135%), ^{44}Ca (2.086%), ^{46}Ca (0.004%) and ^{48}Ca (0.187%). Natural fractionation of Ca isotopes in surface processes is reported to be relatively small (cf. Heumann et al., 1970, 1982; Heumann and Lieser, 1972; Stahl and Wendt, 1968), requiring high analytical precision to be resolved. Stahl and Wendt (1968) and Möller and Papendorff (1971) showed that Ca isotope variations during Rayleigh fractionation must be lower than about 1.5‰/amu. Heumann and Lieser (1972) and later, O'Neil (1986) stated that major Ca isotope fractionation only occurs when materials with ion exchange capacity are involved and that fractionations are proportional to the mass difference, that is, $\delta^{44/40}$Ca is about two times larger than $\delta^{44/42}$Ca. As a consequence, large isotope fractionation effects in an order of up to 22‰ can be observed during ion exchange processes (Heumann, 1972; Heumann and Schiefer, 1980, 1981; Russell et al., 1978). Corless (1968) suggested that variations of Ca isotope ratios of 10‰ (^{48}Ca/(total Ca)) can also be caused by kinetic isotope fractionation introduced by biologically mediated processes. Skulan et al. (1997) were the first who focused their attention on the biological control of the Ca isotopic composition. They analyzed Ca from various marine organisms and concluded that Ca isotope fractionation is relatively uniform in magnitude among vastly different organisms and that Ca becomes isotopically lighter when it moves through food chains. Zhu and MacDougall (1999) suggested that Ca isotope data

from foraminifera of a given species may significantly vary with ocean water temperature and/or depth and showed that there is a 0.6‰ difference in the $\delta^{44/40}$Ca values between *Globigerinoides sacculifer* from the Holocene and the Last Glacial Maximum (LGM) of the equatorial Pacific. The sea surface temperature difference since the Last Glacial Maximum is about 3 °C (Lea et al., 2000), which would lead to the 0.6‰ difference in the isotope values. Such a relationship would indicate a temperature dependence of about 0.2‰/°C for *G. sacculifer*. A more systematic study of $\delta^{44/40}$Ca-temperature relationships in cultured planktonic foraminifera *G. sacculifer* demonstrated a clear temperature dependence over a temperature range from 19.5 to 29.5 °C (Nägler et al., 2000). However, the temperature sensitivity of the Ca isotope fractionation seems to be species-dependent because De La Rocha and DePaolo (2000) claimed that $\delta^{44/40}$Ca ratios of the intertidal foraminifera species *Glabratella ornatissima* are independent of temperature variations. The observation of species-dependent fractionation is supported by Gussone et al. (2003), who investigated temperature-dependent Ca fractionation of cultured *Orbulina universa* (calcite) and inorganically precipitated $CaCO_3$ (aragonite) and concluded that the different fractionation trends of *O. universa* and *G. sacculifer* can be explained by different biochemical fractionation processes related to their calcite precipitation mechanisms.

A major improvement in the precise Ca isotope measurement technique was the application of a double spike by Coleman (1971) and Russell et al. (1978) who first used a ^{42}Ca/^{48}Ca double spike for more accurate measurements of the Ca isotopic composition. They expressed the measured Ca isotope ratios as $\delta(^{40}Ca/^{44}Ca)$ values ($\delta(^{40}Ca/^{44}Ca)= [(^{40}Ca/^{44}Ca)_{sample}/(^{40}Ca/^{44}Ca)_{standard}-1]*1000$) by normalizing the measured ^{40}Ca intensity to ^{44}Ca. A Ca fluorite standard (CaF_2) was used that is supposed to represent average bulk Earth. Skulan et al. (1997) redefined the δ^{44}Ca notation by normalizing the measured ^{44}Ca intensity to ^{40}Ca ($\delta^{44}Ca=[(^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{standard}-1]*1000$).

In single collector TIMS measurements, the intensities of masses 40, 41, 42, 43, 44 and 48 were measured in various sequences on a single Faraday cup using the "peak jumping method". The major disadvantage of this time-consuming method is the

small sample throughput in combination with a reduced internal statistical precision (Skulan et al., 1997). However, recent improvements for Ca isotope measurements have been reported by Heuser et al. (2002) who used a multicollector mass-spectrometer (TIMS) in combination with a modified double-spike technique, improving the statistical uncertainties (internal reproducibility) of Ca isotope measurements and increasing the average sample throughput.

Other mass spectrometers like diode laser resonance ionization mass spectrometry and Multicollector Inductively Coupled Plasma Mass Spectrometry (MC−ICP−MS) (Halicz et al., 1999) have also been tested for Ca isotope analysis. The main problem of the MC−ICP−MS measurements arises from isobaric interferences like $^{40}Ar^+$ on mass 40 or $^{12}C^{16}O_2^+$ on mass 44. In order to overcome this problem, recent progress in the measurement of Ca isotopes using ICP−MS has been demonstrated by Boulyga and Becker (2001) using collision or reaction cells to remove interfering $^{40}Ar^+$.

Here, we report a new technique for the measurement of $^{44}Ca/^{40}Ca$ isotope ratios on MC−ICP−MS using the so-called ''cool plasma'' technique. In contrast to the TIMS technique, Ca isotope measurements on MC−ICP−MS can be performed by the bracketing standard technique and do not require a Ca double spike because the mass bias in the plasma is rather stable compared to the mass-fractionation in the TIMS ion source. This reduces the effort for chemical preparations without any loss of precision and accuracy for the Ca isotope measurements. However, new problems using the ''cool plasma MC−ICP−MS technique'' arise from matrix effects related to the Ca bulk solution and isobaric effects with MgO^+, $MgOH_2^+$ and $NaOH^+$, respectively. To test the reproducibility and precision of the new method, we measured NIST SRM 915a, Johnson Matthey standards lot 4064 and lot 9012 inorganically precipitated aragonite and cultured *O. universa* samples. Our cool plasma MC−ICP−MS results are in general accord with previously published TIMS data. Note that following Hippler et al. (2003) and the discussion at the EUG−EGS−AGU Joint Assembly in Nice in 2003, with members from various European laboratories measuring Ca isotope fractionation, we agreed to apply NIST SRM 915a for normalization and to use the following δ-notation for all Ca data pre-

sented in this work: $\delta^{44/40}Ca=[(^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{NIST\ SRM\ 915a}-1]*1000$ (Eisenhauer et al., in press). The intention of the latter notation is to clearly distinguish isotope measurements normalized to ^{42}Ca and ^{40}Ca, respectively.

2. Material and methods

2.1. Standards and chemical preparation

For this study, we analyzed NIST SRM 915a, Johnson Matthey $CaCO_3$ standards lot 4064 and 9912, inorganically precipitated aragonite and *O. universa* (calcitic foraminifer). These samples and standards were already characterized in TIMS studies (Russell et al., 1978; Heuser et al., 2002; Gussone et al., 2003; Hippler et al., 2003; Schmitt et al., 2003). Cleaning procedures for the foraminifera, chemical preparation and interpretation of the $\delta^{44/40}Ca$ measurements are presented in detail in Gussone et al. (2003). For MC−ICP−MS measurements, the NIST SRM 915a standard material as well as the two Johnson Matthey $CaCO_3$ standards (lot No. 4064 and lot No. 9912) were prepared from 300 ppm stock solutions and diluted to a concentration of about 3 ppm in 5% nitric acid solution. The inorganic aragonite and cultured *O. universa* samples were originally dissolved in 2N HCl for TIMS analysis. These solutions with concentrations of 40 ppm Ca (inorganic precipitates) and 8 ppm (*O. universa*) were further diluted with 5% nitric acid to a concentration of 3 ppm prior to MC−ICP−MS analyses. As a consequence of the differences in the original Ca concentration, the remaining amount of HCl in the *Orbulina* samples was five times higher than in the aragonite samples. A Ca concentration of about 3 ppm corresponds to a beam intensity of about 5 V on ^{40}Ca, which is 500-fold above the ^{40}Ar background and well below the maximum intensity the cups can handle (10 V). We chose this Ca concentration (this beam intensity) for all our measurements. Monitoring the Ar signal, we found the Ar background to be fairly stable varying less than 5% during the day.

All standards and samples were introduced into the Ar-plasma source through a water-cooled cyclonic spray chamber combined with a MicroMist-100 (Glass Expansion) self-aspiring microconcentric nebulizer

with a sample uptake rate of 100 μl/min. This setting for the sample introduction combines low sample consumption, relatively short wash out time, stable aerosol generation and reduced matrix effects, and thus reduces the abundance of interfering molecular species.

2.2. Mass spectrometry and cool plasma technique

Ca isotope ratios were measured using an AXIOM MC–ICP–MS (ThermoElemental, Winsford, UK). This instrument is a double-focusing magnetic sector field instrument equipped with eight variable Faraday collectors and one fixed collector in the focal plane. In addition, it is equipped with a special Faraday cup at the high-energy side in order to account for the entire mass dispersion of Ca isotope masses from 40 to 48 amu.

Using a hot plasma with 1250 W radio frequency (RF) power, $^{44}Ca/^{40}Ca$ ratios cannot be measured because of an irresolvable isobaric interference of $^{40}Ar^+$(39.96238 amu) with $^{40}Ca^+$(39.96259 amu). Under normal measurement conditions, the $^{40}Ar^+$ ion intensity corresponds to about 0.5 V. In order to separate $^{40}Ar^+$ from $^{40}Ca^+$, a mass resolution of 190,500 Res is required, being much higher than the presently available mass resolution of the AXIOM mass spectrometer of about 10,000 Res. Thus, to measure the $^{40}Ar^+$-free $^{44}Ca/^{40}Ca$ isotope ratio, the $^{40}Ar^+$ signal has to be significantly reduced. For our MC–ICP–MS system, this can be done with the so-called cool plasma technique, reducing the radio frequency (RF) power from 1250 to about 400 W. At least 320 W RF power were found to be necessary to supply the plasma with energy. The operating conditions for the calcium isotope measurements that are described for the cool plasma technique are given in Table 1.

The reduction of the RF energy reduces the $^{40}Ar^+$ intensity by a factor of about 50 to about 0.01 V. For example, in the "hot plasma mode", a ^{40}Ca peak of 5 V corresponds to a $^{40}Ar^+/^{40}Ca^+$ ratio of about 0.1. The latter ratio would significantly reduce to about 0.002 in the cool plasma mode (Fig. 1A and B). The intensity of Ar background depends on the type of sample introduction system used in front of the MC–ICP–MS. Using a desolvating device (Cetac ARIDUS), producing a dry aerosol consumes less energy compared to a more "wet" aerosol produced by the conventional glassware. In the latter case, ^{40}Ar is less

Table 1
AXIOM cool plasma settings

Gases (l/min)	Cool	14.0
	Aux	0.4
	Neb	0.8
Torch setting	X	− 110
	Y	105
	Z	− 100
Potential (V)	Acc. voltage	4960
	Transfer 1	3660
	Transfer 2	3150
	X deflect 1	40
	Y deflect 1	5
	X lens	− 2450
	Rotate	0
	Curve	0
	X deflect 2	− 2
	Y deflect 2	− 20
	Y deflect 3	− 1
RF power (W)	Ignite	1200
	Shield out	400
Resolution (m/Δm)		430

Note the difference in the torch position for cool plasma ($Z = − 100$) in contrast to hot plasma ($Z = 100$).

effectively ionized resulting in a much lower intensity (about 0.5 V), while with a dry aerosol, the intensity of ^{40}Ar is high enough to saturate the Faraday cup (more than 10 V). In the case of our machine setting, the mass spectra are dominated by ArH^+ rather than by pure Ar^+. The change to cool plasma conditions strongly suppresses the most important Ar-related interferences like Ar^+, ArH^+ and ArD^+ (Fig. 1B). However, beside the Ar^+-compounds, there are further interferences in the calcium isotope mass range such as $^{14}N_2^{16}O^+$, $^{12}C^{16}O_2^+$ and $^{26}Mg^{16}OH_2^+$ on ^{44}Ca and of $^{24}Mg^{16}O^+$, $^{23}Na^{16}OH^+$ on ^{40}Ca. These possible interferences can be monitored in the high-mass resolution mode at about 8000 Res. The only interferences found to be relevant for ^{40}Ca (39.962 amu) are $^{24}Mg^{16}O^+$ (39.97995 amu) and $^{23}Na^{16}OH^+$ (39.9925 amu) and for ^{44}Ca (43.95554 amu) $^{26}Mg^{16}OH_2^+$ (43.99316 amu; Fig. 2A and B). In order to overcome these interference problems, we measured the Ca intensity not at the peak center but 0.02 amu shifted away from the center towards the low-mass side of the peak. At this point, the measurement is still at the top of the flat Ca peak plateau but out of the influence of the interfering molecular species (Fig. 2C). In order to achieve the
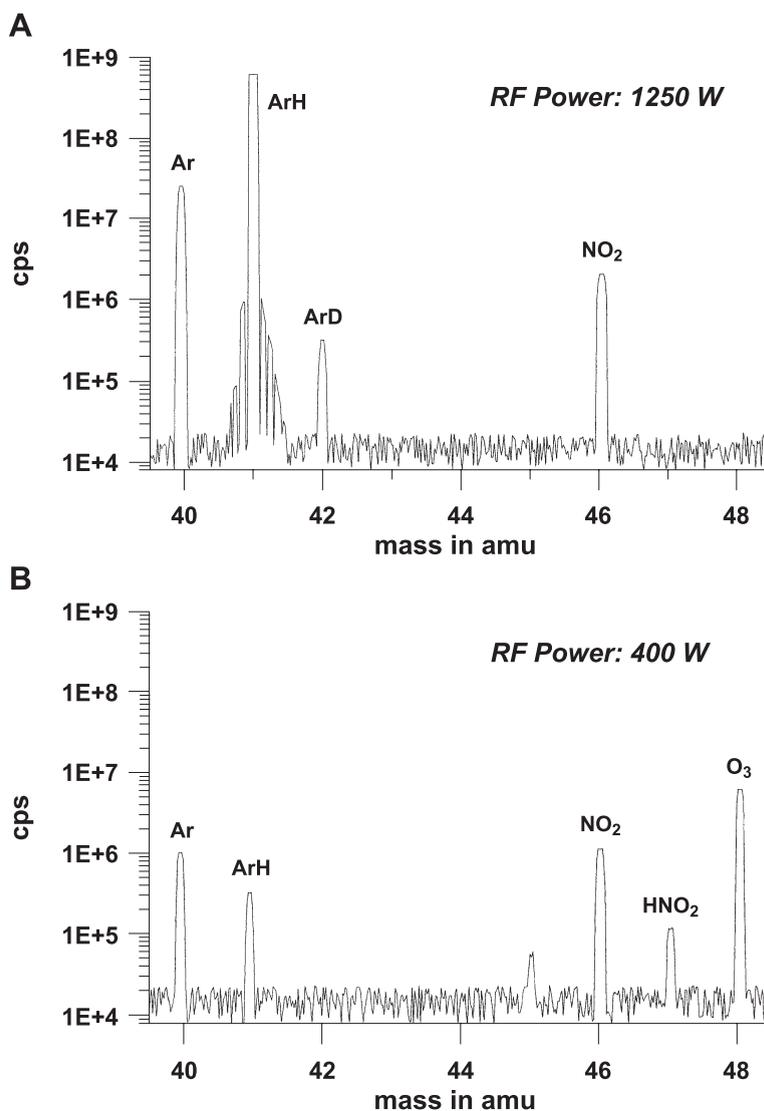
Fig. 1. The background peak intensity is shown as a function of mass in the range from 40 to 48 amu. It can be seen that the $^{40}Ar^+$ intensity is significantly lower after reduction of the RF power from 1250 (A) to 400 W (B).

best results, it is very important to tune the instrument for the optimum peak shape. In particular, a flat top peak with at least 0.04 amu plateau width is required. Our AXIOM MC–ICP–MS system usually produces flat peak tops of about 0.046 amu at a working mass resolution of about 400 Res. Other possible interferences are related to $^{88}Sr^{2+}$ and $^{86}Sr^{2+}$ ions interfering with ^{44}Ca and ^{43}Ca. The latter interferences can be monitored measuring beam intensities at 43.5 amu corresponding to $^{87}Sr^{2+}$. For all standards and sam-

ples measured in this study, no significant Sr-related interferences were found.

It is well known that the cones strongly influence the mass fractionation in the interface. We found that the best performance was reached by a combination of a standard sample cone and a RAC19 skimmer cone (0.5-mm diameter). In this case, mass fractionation was smaller than 1%/amu in the Ca mass range. This is in sharp contrast to approx. 3% per mass unit using a standard skimmer cone.
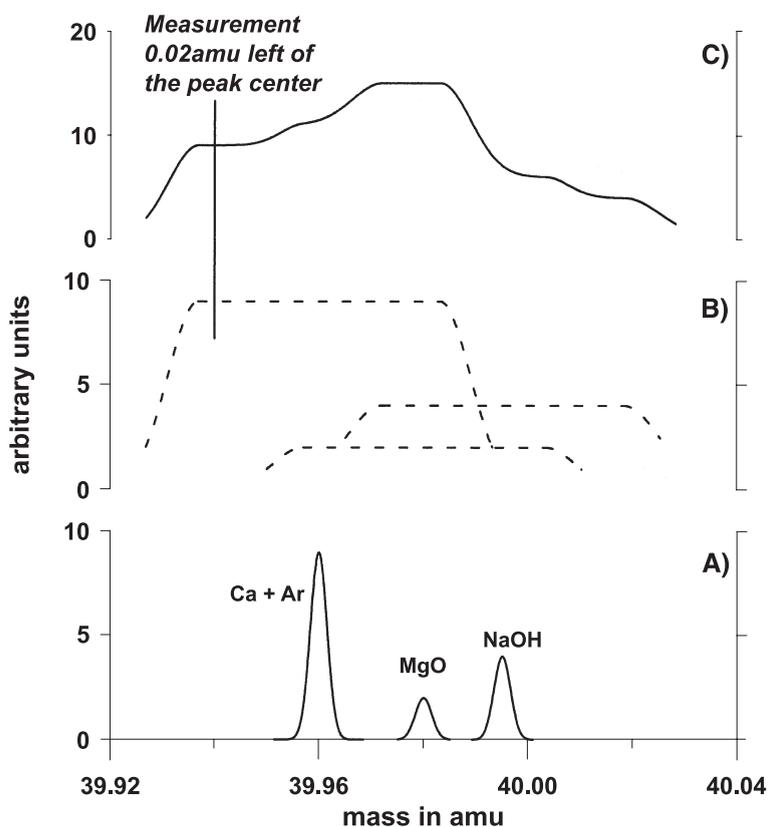
Fig. 2. Schematic drawing showing possible interfering atomic and molecular masses at 40 amu. Peak intensities are presented in arbitrary units as a function of atomic mass. (A) Using high-mass resolution (8000 Res), interfering molecular peaks can clearly be distinguished. (B) Same peaks at low-mass resolution (400 Res). (C) Integral peak plateau at 40 amu at low-mass resolution (400 Res). The mass setting used for data acquisition (0.02 towards the low-mass side of the peak center) is indicated by a vertical line. This mass setting is still on the top of the ^{40}Ca (resp. ^{40}Ar) peak but outside the range of the interfering molecular interferences.

Furthermore, we observed that the Ca isotope measurements strongly depend on the acid and its normality used for sample digestion. Different acids and normalities resulted in reproducible mass fractionation offsets (see also Section 3.3). In order to achieve reproducible standard, sample and background measurements, we always used a 5% nitric acid solution for sample preparation and dilution.

3. $\delta^{44/40}$Ca measurements using the cool plasma technique

In order to demonstrate that the cool plasma technique produces reliable and reproducible results, ^{44}Ca/^{40}Ca measurements on NIST SRM 915a stan-

dard material have been performed. For these measurements, we adopted the standard–sample–standard bracketing technique accounting for the mass bias and also permitting correction for instrumental drift. During data acquisition, the intensities at 40, 42 and 44 amu were collected 100 times (3 s each) in static mode. Prior to the sample measurements, clean wash solution (5% nitric acid) was analyzed to determine background values. These background values were taken to correct the data for detector baselines, Ar$^+$ contribution to 40 amu and Ca blanks. In addition, 43.5 amu was monitored in order to verify the presence/absence of ^{87}Sr^{2+} ions. After each sample, pure 5% nitric acid was introduced to wash out the tubing, nebulizer and spray chamber. A wash out time of 2 min is sufficient because usually, after

about 60 s, the Ca ion intensity decreases to less than about 1%.

3.1. Standard materials (NIST SRM 915a, Johnson Matthey [lot 4064 and 9912)]

In Fig. 3, the $^{44}Ca/^{40}Ca$ isotope ratios of NIST SRM 915a were normalized to themselves using the standard–sample–standard bracketing technique. The reproducibility of the $\delta^{44/40}Ca$ values over a period of 8 weeks comprising 83 single measurements was found to be about 0.14‰ RSD. This reproducibility is similar to TIMS measurements using a $^{43}Ca/^{48}Ca$ double spike (0.18‰ RSD; Heuser et al., 2002). However, the big advantage of the new technique is an up to four times higher sample throughput and a simplification of the chemical preparation and data reduction because no Ca double spike is required anymore.

In addition, 12 and 11 measurements were performed on the Johnson Matthey lot 4064 and 9012 standard material, respectively (Fig. 4A and B). $\delta^{44/40}Ca$ values of $-11.29‰$ and $0.57‰$ were determined for lot 4064 and 9012, respectively. Both values agree within error with the values of

Fig. 4. MC–ICP–MS $\delta^{44/40}Ca$ measurements of the two Johnson Matthey $CaCO_3$ standards, lot 4064 (A) and 9912 (B) previously used by Heuser et al. (2002) and Russell et al. (1978). The previously determined difference in $\delta^{44/40}Ca$ of about 12‰ between these two standards is reproduced by the MC–ICP–MS measurements.
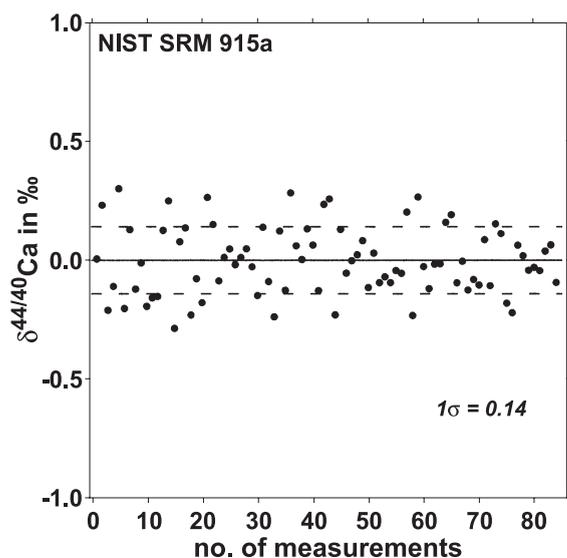
Fig. 3. MC–ICP–MS $\delta^{44/40}Ca$ measurements of NIST SRM 915a normalized to itself. Horizontal line marks the zero mean value. Dashed lines mark the 1σ standard deviation of 0.14.
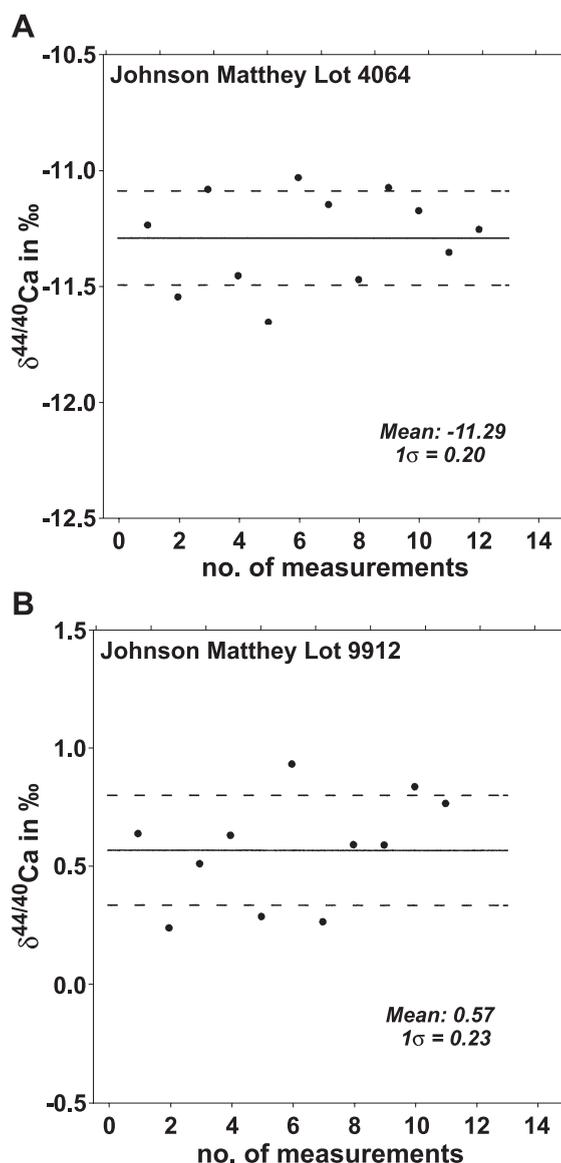
$-11.38‰$ and $0.63‰$, previously determined by conventional TIMS technique (Heuser et al., 2002; Hippler et al., 2003; Schmitt et al., 2003, Russell et al., 1978). Both standards are, in particular, impor-

tant because they demonstrate that the relative difference of about 12‰ is correctly reproduced by our MC–ICP–MS measurements.

3.2. Samples [inorganically precipitated aragonite and O. universa (calcite)]

In order to extend our tests of the new cool plasma MC–ICP–MS technique and to verify the temperature dependency of the $\delta^{44/40}$Ca values previously observed in carbonates (Skulan et al., 1997; Zhu and MacDougall, 1999; Nägler et al., 2000; Gussone et al., 2003), we measured $\delta^{44/40}$Ca values on calcitic foraminifer and aragonitic precipitates (Table 2). The precipitation of the aragonite samples under controlled temperature conditions has been described by Gussone et al. (2003). In addition, the culturing of *O. universa* under controlled conditions is extensively discussed in Spero et al. (1997). Both sample materials are of particular interest because precise TIMS $\delta^{44/40}$Ca data have been reported and discussed by Gussone et al. (2003).

3.2.1. Inorganically precipitated aragonite
From Fig. 5, it can be seen that the MC–ICP–MS-based measurements of the $\delta^{44/40}$Ca values of the inorganic precipitates are indistinguishable from the TIMS $\delta^{44/40}$Ca measurements of Gussone et al. (2003). Both mass spectrometric techniques clearly show a $\delta^{44/40}$Ca-temperature relationship of about 0.016‰/°C. The close agreement of the TIMS- and MC–ICP–MS-based $\delta^{44/40}$Ca measurements is a further verification of the earlier observed temperature-dependent Ca isotope fractionation.
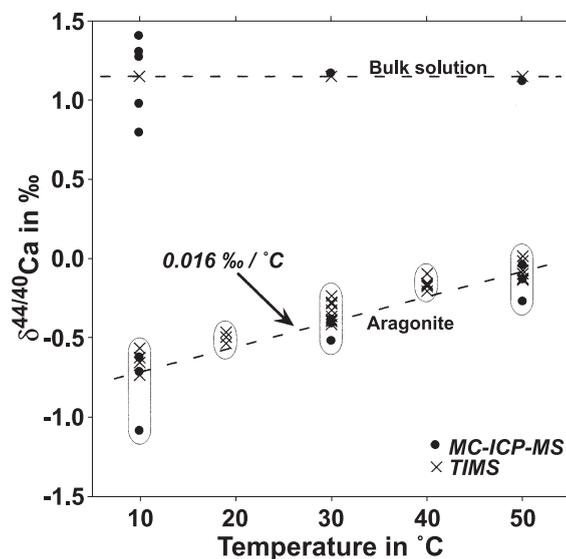

Fig. 5. MC–ICP–MS-based $\delta^{44/40}$Ca and TIMS-based $\delta^{44/40}$Ca values of inorganically precipitated CaCO$_3$ (aragonite; Gussone et al., 2003) are shown as a function of temperature. Within statistical uncertainties, the values of both measurements are indistinguishable from each other.
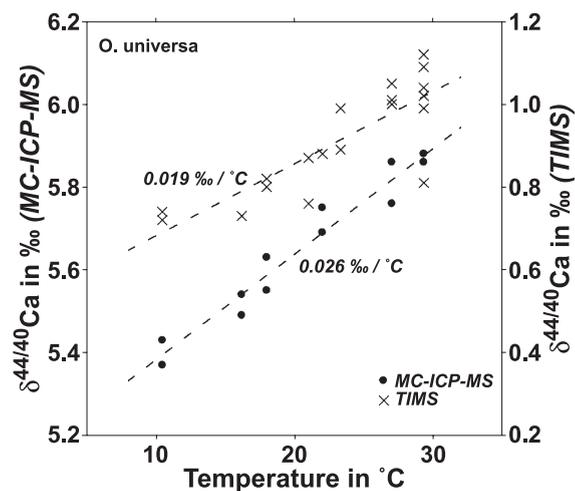
Table 2
$\delta^{44/40}$Ca [‰] at different temperatures in *O. universa* and inorganically precipitated aragonite

Inorganic aragonite			O. universa					
10 °C	30 °C	50 °C	10.5 °C	16.2 °C	18 °C	22 °C	27 °C	29.3 °C
− 0.71	− 0.40	− 0.27	5.37	5.49	5.55	5.69	5.75	5.88
− 1.08	− 0.39	− 0.04	5.43	5.54	5.63	5.75	5.76	5.86
− 0.62	− 0.38	− 0.13						
− 0.71	− 0.51							

Note: $\delta^{44/40}$Ca [‰] =[(^{44}Ca/^{40}Ca)$_{sample}$/(^{44}Ca/^{40}Ca)$_{NIST\ SRM\ 915a}$ − 1]1000.

Fig. 6. MC–ICP–MS-based $\delta^{44/40}$Ca and TIMS-based $\delta^{44/40}$Ca values of *O. universa* samples (calcite; Gussone et al., 2003) are shown as a function of temperature. The MC–ICP–MS-based $\delta^{44/40}$Ca-temperature gradient is steeper than the TIMS-based $\delta^{44/40}$Ca gradient. Note that there is an offset between the MC–ICP–MS- and the TIMS-based $\delta^{44/40}$Ca values of about 5‰ caused by a matrix effect.

3.2.2. O. universa

The TIMS- and MC–ICP–MS-based $\delta^{44/40}Ca$ measurements of *O. universa* tests show slightly different slopes of 0.019‰/°C and 0.026‰/°C, respectively. However, the most critical observation is that a large $\delta^{44/40}Ca$ offset of about 5‰ (at 10 °C) is observed between the techniques (Fig. 6). This $\delta^{44/40}Ca$ offset is attributed to a so-called matrix effect because, in contrast to the inorganic precipitates, the chemical composition and the acidity of the analyzed solution of the *O. universa* tests were significantly different from the chemical composition and acidity of the standard solutions (see Section 2.1).

3.3. Influence of matrix and acidity on the $\delta^{44/40}Ca$ ratios

Differences in chemical composition are well known to be crucial for the accuracy of the MC–ICP–MS measurement because the ion abundance in the plasma sensitively controls the instrumental mass fractionation, and thus, the measured isotope ratios. In addition, the chemical composition of the sample also strongly affects the formation of isobaric interferences in the plasma. In order to study this matrix effect and to verify whether or not such effects can be corrected for, we dissolved NIST SRM 915a in 5% nitric acid and prepared subsequently solutions by the addition of 9%, 4.5% and 2.3% of HCl. From Fig. 7, it can be seen that the $\delta^{44/40}Ca$ ratios increase as a function of the increasing HCl content from about 0‰ to about 30‰. Interpolation of the measured $\delta^{44/40}Ca$ ratio indicate that a content of about 0.7% HCl corresponds to a $\delta^{44/40}Ca$ ratio offset of about 5‰. The latter value is in general accord with our result from the *O. universa* measurements, indicating that isotopic offsets caused by matrix variation is reproducible. In particular, these measurements demonstrate the high sensitivity of Ca isotope measurements on MC–ICP–MS from the sample and standard matrix.

4. Summary and conclusions

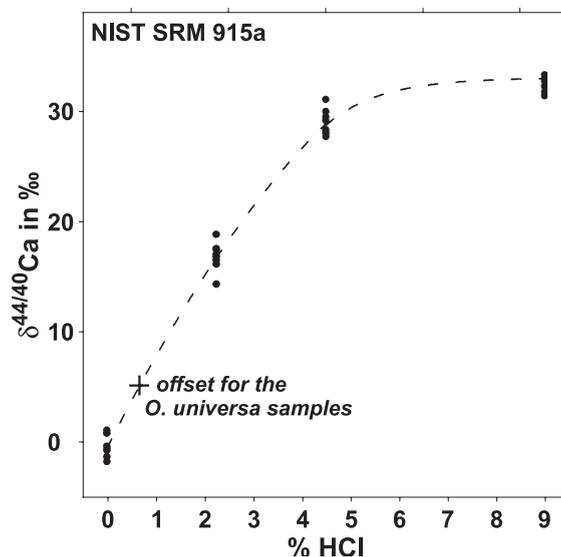$^{44}Ca/^{40}Ca$ ratios can be precisely and reproducibly measured by MC–ICP–MS using the cool plasma technique.

Fig. 7. This figure shows $\delta^{44/40}Ca$ ratios as a function of HCl added to a 5% nitric acid solution of NIST SRM 915a. It can be seen that the $\delta^{44/40}Ca$ values increase as a function of the amount of HCl added to the standard. Then, latter function can be used to correct for the observed matrix effect in the *O. universa* samples.

TIMS-based $\delta^{44/40}Ca$ and MC–ICP–MS $\delta^{44/40}Ca$ values are in general accordance.

Internal precision of MC–ICP–MS $\delta^{44/40}Ca$ measurements is similar to TIMS.

Reproducible and accurate $\delta^{44/40}Ca$ measurements on MC–ICP–MS using the cool plasma technique require constant Ca concentration in the solution, a constant acid normality and a reproducible sample matrix.

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