Nano-SIMS Analysis of Mg, Sr, Ba and U in Natural Calcium Carbonate

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Concentrations of minor (Mg and Sr) and trace (Ba and U) elements in four natural calcium carbonate samples were first analyzed by inductively coupled plasma mass spectrometry (ICP-MS) after chemical dissolution and calibrated against a standard dolomite. Their homogeneities were checked by *in situ* laser ablation (LA) ICP-MS with 10–20 spots. The carbonate samples were measured by using a high lateral resolution secondary ion mass spectrometer (Nano-SIMS NS50). A ~4 nA O⁻ primary beam was used to sputter a 5–6-μm diameter crater on the sample surface, and secondary positive ions were extracted for mass analysis using an accelerating voltage of 8 kV and a Mattauch-Herzog geometry. A multi-collector system was adjusted to detect ²⁶Mg⁺, ⁴³Ca⁺, ⁸⁸Sr⁺, ¹³⁸Ba⁺, ²³⁸U¹⁶O⁺ and ²³⁸U¹⁶O₂⁺ ions at the same time. A resolving power of 2500–5000 at 10% peak height was attained by an entrance slit set at 40 μm, and each exit slit at 50 μm with adequate flat-topped peaks. The observed ²⁶Mg/⁴³Ca, ⁸⁸Sr/⁴³Ca, ¹³⁸Ba/⁴³Ca and ²³⁸U¹⁶O₂/⁴³Ca ratios agreed well with those measured by LA-ICP-MS. Foraminifera shells were analyzed at 5–6 μm scale by Nano-SIMS. There was a large variation of the Mg/Ca ratios, up to ±38%, even in a single fragment of the shell, suggesting that although the ratios provide a useful paleoceanographic proxy at bulk scale, they may reflect a more complex pattern at <10 μm scale.

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Introduction

In paleoclimate studies, valuable information, such as ancient ocean temperatures^{1–3} and past alkalinity distributions,⁴ can be derived from the study of minor (Mg and Sr) and trace (Ba and U) element concentrations in marine calcium carbonates. These effects are attributable to the fact that Mg, Sr and Ba are members of Group II in the periodic table, and all have very similar chemical and physical properties, including a stable 2+ oxidation state. However, they do not behave identically in nature, and their differences in behavior have significant implications in geochemistry. For example, laboratory experiments have shown that the partition coefficient of Mg²⁺ into inorganic calcite correlates strongly with temperature.⁵ Recent studies have revealed that the U/Ca ratios in corals could provide a temperature proxy comparable in accuracy to the Sr/Ca ratios.⁶ The mechanism may be ascribed to a recent study⁷ showing that the uranyl ion (UO₂²⁺) substitutes easily for Ca²⁺ in aragonite. In addition, the Ba/Ca ratio of biogenic carbonate has been used to reconstruct past alkalinity distributions in oceans.⁴

There are several analytical methods that can be applied to measuring these elements at the ~50 μm scale in calcium carbonate, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS) and electron microprobe (EMP). Among

them, the LA-ICP-MS method⁸ has a number of advantages, such as being easy to operate, less expensive and having a smaller matrix effect than the SIMS method.⁹ However, LA-ICP-MS consumes more sample (has worse depth resolution) and it is difficult to reduce the probe spot to <10 μm to achieve greater sensitivity. On the other hand, the advantages of the EMP method¹⁰ are its relatively low cost and excellent spatial resolution (spot size ~3 μm) compared with the SIMS method, while the major drawback of the EMP is its relatively low sensitivity, whereby it is impossible to detect trace elements at the several 10s μmol/mol level.

The most powerful tool for precise trace-element analysis of calcium carbonate is the SIMS method with its significant depth resolution.⁹ Recently, a Nano-SIMS NS50 ion microprobe with unparalleled lateral resolution up to 0.05 μm has been developed by Cameca¹¹ and mostly applied to the field of cosmochemistry,^{12,13} with few geochemical applications thus far.^{14,15} It is desirable to apply this new ion microprobe to the analysis of terrestrial samples with its high lateral resolution.

In this work, minor (Mg and Sr) and trace (Ba and U) element analysis of natural calcium carbonate was carried out by using a Nano-SIMS NS50 instrument. Experimental details of the ion microprobe measurements at spot size of 5–6 μm are given. We assessed the accuracy and precision of the analyses as compared with those determined by ICP-MS after chemical dissolution, and also those determined by LA-ICP-MS on the same samples measured by Nano-SIMS. We then applied this method to foraminifera, which are tiny single-celled marine organisms that construct calcium carbonate shells.

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Experimental

Samples

Five natural calcium carbonate samples were prepared. They were named JDo-1, LAS20, NBS19, TN2349 and SPA4. JDo-1 is a dolomite standard collected from Kuzuu-machi, Tochigi Prefecture, central Japan and distributed by the Geological Survey of Japan¹⁶ for a reference of sedimentary rock. LAS20 and SPA4 are both U-rich calcite with thick aragonite rims extracted from a 13700 year old speleothem deposit in the Vinschgau Valley of northernmost Italy.¹⁷ NBS19 is a calcite standard derived from a limestone of unknown origin and distributed by the US National Bureau of Standards for carbon isotope measurements.¹⁸ TN2349 is a 35 million year old calcite from a Mississippi Valley-type zinc ore deposit.¹⁹ Planktonic foraminiferal shells were collected by a box core in the western equatorial Pacific by the KH92-1 cruise of the Research Vessel, Hakuho Maru of the Ocean Research Institute, the University of Tokyo. The species was identified as *Globigerinoides sacculifer*, which is generally abundant in tropical water masses.²⁰

ICP-MS solution analysis

Calcium carbonate samples were crushed and homogenized, and then aliquots weighing about 5 mg were dissolved by HNO₃ and diluted so that the Ca concentrations were 2.0 ± 0.3 ppm. The abundances of Mg, Sr, Ba and U were determined by ICP-MS (ThermoElectron VG PlasmaQuad 2) installed at Department of Earth and Planetary Sciences, Tokyo Institute of Technology. It was confirmed that the isotopic compositions of Mg, Ca, Sr and Ba agreed with those of reference values. In actual analysis, the quadrupole mass spectrometer was cyclically peak-stepped through a series of mass numbers, (26, 43, 88, 138 and 238) to measure the ^{26}Mg , ^{43}Ca , ^{88}Sr , ^{138}Ba and ^{238}U intensities by using an ion counting detector with 10 s integrations. The observed $^{26}\text{Mg}/^{43}\text{Ca}$, $^{88}\text{Sr}/^{43}\text{Ca}$, $^{138}\text{Ba}/^{43}\text{Ca}$ and $^{238}\text{U}/^{43}\text{Ca}$ ratios of four samples (LAS20, NBS19, TN2349 and SPA4) were calibrated against those of JDo-1 with certified abundances after subtracting blanks measured on deionized water prepared by using Milli-Q SP ICPMS Spec.

Laser ablation ICP-MS analysis

Calcium carbonate grains were cast into an epoxy resin disc together with two chips of NIST standard silicate glasses (SRM610 and 612). The samples were polished until the mid-sections of the chips were exposed. Final polishing was made with 0.25 μm diamond paste. For elemental analysis using LA-ICP-MS, the laser ablation sample introduction technique was applied in this study.²¹ The laser ablation system used in this study was a MicroLas Laser Ablation System (Gottingen, Germany) GeoLas 200CQ.²² This system utilizes a Lambda Physik (Gottingen, Germany) COMPex 102 ArF excimer laser operating at 193 nm. He gas instead of Ar gas was used as a carrier gas, which improved the sample transport efficiency from the sample cell to ICP, and reduced the sample desorption around the ablation pit.²³ The resulting instrumental sensitivity was about $> 400 \text{ Hz}/\mu\text{g g}^{-1}$ for the analyses, when an ablation pit size of 16 μm , and a laser emission power of 2 mJ with repetition rate of 5 Hz were applied. The typical drilling rate observed here was 0.5 $\mu\text{m/s}$, and therefore, the resulting depth of the ablation pit was 5–8 μm after the analysis sequence (15 s) under the conditions, such as the laser power and repetition rate, employed in this study. In order to minimize the elemental fractionation and to improve the repeatability in the elemental

Fig. 1 Configuration of the multi-collector system of Nano-SIMS. The ion counting detectors, EM#1 – EM#4 are movable on a trolley, while EM#5 and LD are fixed. It is possible to detect $^{26}\text{Mg}^+$, $^{43}\text{Ca}^+$, $^{88}\text{Sr}^+$, $^{138}\text{Ba}^+$, $^{238}\text{U}^{16}\text{O}^+$ and $^{238}\text{U}^{16}\text{O}_2^+$ ions at the same time. Deflectors are located immediately before each exit slit.

ratio measurement achieved by the LA-ICPMS, a stabilizer device was applied.²⁴ The stabilizer device acted as a particle filter, which could minimize the introduction of large aerosol particles into the ICP, which could cause a spiky and unstable signal intensity. The resulting ablation pit size was 18 μm , obtained through data integration (20 s/spot). The experimental settings of the ICP-MS were the same as those of solution analysis. The observed data were again calibrated against those of JDo-1.

Nano-SIMS

Planktonic foraminiferal shells were cast into an epoxy resin disc together with a grain of LAS20 calcite and two chips of NIST standard silicate glasses (SRM610 and 612). The samples were polished until the mid-sections of the shells and chips were exposed. Final polishing was made with 0.25 μm diamond paste to provide a flat surface for the sputtering of secondary ions, and the disc surface was carbon-coated. Images of the sample were determined by an electron microprobe (EMP) to locate inclusion-free homogeneous regions suitable for analysis. It was then slightly polished again to remove the carbon coat and damaged layer of the EMP. Prior to analysis, the foraminifera mount as well as the carbonate mount were cleaned with petroleum spirits, detergent and pure water to reduce the surface contaminants, and then gold coated to dissipate any charge during the analysis.

There are two crucial advantages of Nano-SIMS over any conventional SIMS. First, the co-axial mode of primary and secondary beams gives a short working distance of the probe forming lens/extraction system, resulting in a smaller spot size for a provided beam current. Second, the multi-collector system with a Mattauch-Herzog geometry covers a wider range of mass numbers (Fig. 1). In the present study, we could detect ^{26}Mg (by an ion-counting detector, called EM#1, which could move on the trolley and be set at a radius (R) of 170.9 mm), ^{43}Ca (EM#2; set at $R = 219.5$ mm), ^{88}Sr (EM#3; set at $R = 313.9$ mm), ^{138}Ba (EM#4; set at $R = 394.3$ mm), $^{238}\text{U}^{16}\text{O}$ (EM#5; position fixed at $R = 533.2$ mm) and $^{238}\text{U}^{16}\text{O}_2$ (LD; fixed at $R = 549.8$ mm) at the same time under a static magnetic field. The entrance and exit slits (EM#1 – #5 and LD) were set to about 40 μm and 50 μm each, respectively.

The samples were evacuated in an air lock overnight and

Fig. 2 Mass spectra around the $^{26}\text{Mg}^+$ (a) and $^{88}\text{Sr}^+$ (b) peaks of natural calcium carbonate, LAS20. The spectra were obtained by deflector voltage scanning under a static magnetic field. The mass resolving power is variable dependent on the detector position.

introduced into a sample stage in the ion source chamber of a Nano-SIMS installed at the Ocean Research Institute, the University of Tokyo. A mass-filtered ~ 4 nA $^{16}\text{O}^-$ primary beam was used to sputter a 5–6- μm diameter crater on the sample surface, and secondary positive ions were extracted for mass analysis using an accelerating voltage of 8 kV. The focusing conditions of ions may have been slightly different from one detector to the other, depending on the trolley position (Fig. 1), which would sometime lead to a different mass resolving power under the static magnetic field. Figure 2 shows the mass spectra around (a) $^{26}\text{Mg}^+$ and (b) $^{88}\text{Sr}^+$ peaks of LAS20 calcite obtained by a deflector located immediately before the exit slit with a voltage scan. It is noted that the ion source condition and magnetic field were identical. A resolving power of 3100 was attained at 10% peak height of $^{26}\text{Mg}^+$ ($R = 170.9$ mm), where the interference of $^{13}\text{C}_2^+$ was negligibly small, while the resolving power of 5240 was taken at $^{88}\text{Sr}^+$ ($R = 313.9$ mm), which showed a small side peak of $^{40}\text{Ca}^{16}\text{O}_3^+$. Before the actual analysis, the sample surface was rastered for 3 min in order to clean off any possible contaminants. It was checked that the isotopic compositions of Mg, Ca and Sr agreed with those of the reference values by magnet scanning, even though that of Ba in TN2349 was discrepant from the reference. We measured the ^{26}Mg , ^{43}Ca , ^{88}Sr , ^{138}Ba and $^{238}\text{U}^{16}\text{O}$ and $^{238}\text{U}^{16}\text{O}_2$ intensities of the samples by using ion-counting detectors (EM#1–5 and LD) with 10 s integrations under a static magnetic field. It took about 10 min to complete a single analysis, including the surface rastering and 50 ratio measurements. The observed data of four samples (LAS20, NBS19, TN2349 and SPA4) were calibrated against those of JDo-1. The $^{26}\text{Mg}/^{43}\text{Ca}$, $^{88}\text{Sr}/^{43}\text{Ca}$, $^{138}\text{Ba}/^{43}\text{Ca}$ and $^{238}\text{U}^{16}\text{O}_2/^{43}\text{Ca}$ ratios of NIST standard silicate glasses (SRM610 and 612) were also determined in the same manner as calcium carbonate samples.

Results and Discussion

Calcium carbonate

Table 1 lists the Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios of four natural calcium carbonate samples measured by ICP-MS after chemical dissolution. The errors are one sigma, estimated by the reproducibility of 10 measurements as well as those of a standard sample (JDo-1) combined in quadrature. The precision is less than 5% for the minor elements and 10% for the trace

Table 1 Minor and trace elements in calcium carbonate samples measured by ICP-MS after chemical dissolution

Sample	Mg/Ca mmol/mol	Sr/Ca mmol/mol	Ba/Ca $\mu\text{mol/mol}$	U/Ca $\mu\text{mol/mol}$
JDo-1 ^a	757	0.219	7.38	0.595
LAS20	31.10 ± 0.95	0.595 ± 0.009	18.42 ± 0.99	119.3 ± 7.4
NBS19	13.04 ± 0.64	0.199 ± 0.006	2.41 ± 0.24	0.34 ± 0.05
TN2349	3.62 ± 0.15	0.101 ± 0.002	—	10.30 ± 0.67
SPA4	3.20 ± 0.16	1.437 ± 0.023	11.44 ± 0.47	74.74 ± 4.59

a. From GSJ Geochemical Reference samples DataBase (<http://www.aist.go.jp/RIODB/geostand>)

Errors are one sigma.

Table 2 Minor and trace elements in calcium carbonate samples measured by *in situ* LA-ICP-MS

Sample	Mg/Ca mmol/mol	Sr/Ca mmol/mol	Ba/Ca $\mu\text{mol/mol}$	U/Ca $\mu\text{mol/mol}$
JDo-1 ^a	757	0.219	7.38	0.595
LAS20	28.70 ± 1.20	0.580 ± 0.024	18.16 ± 1.08	121.40 ± 11.90
NBS19	14.05 ± 1.16	0.176 ± 0.043	2.03 ± 0.63	—
TN2349	3.66 ± 0.29	0.089 ± 0.025	0.17 ± 0.10	14.38 ± 3.10
SPA4	2.38 ± 0.23	1.238 ± 0.300	11.53 ± 3.29	78.39 ± 21.59

a. From GSJ Geochemical Reference samples DataBase (<http://www.aist.go.jp/RIODB/geostand>)

Errors are one sigma.

elements, except for the U/Ca ratio of NBS19. The Ba/Ca ratio of TN2349 was not obtained because of its lower abundance than the detection limit.

Table 2 lists the Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios of four natural calcium carbonate samples measured by LA-ICP-MS. Analysis spots with 30 μm diameter were randomly selected on the surface. The errors are one sigma, estimated by the reproducibility of 10–20 spot measurements as well as those of a standard sample (JDo-1) combined in quadrature. The precision is 5%–30%, except for the Ba/Ca ratio of TN2349, and generally larger than those of the solution analysis. The U/Ca ratio of NBS19 was not obtained because of the low U abundance.

Taking into account the error, the observed Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios measured by solution analysis agree well with those measured by LA-ICP-MS, suggesting that the accuracy of the measurement is acceptable. The relatively large errors of the LA-ICP-MS method may be attributable to either the lateral heterogeneity of the samples and/or smaller intensities of the measured ions. For example, the U intensity of NBS19 was about 30 cps, which was equivalent to background level, while that of SPA4 was large with a value of 43000–69000 cps. In the latter case, the sample heterogeneity is dominant reason of the error. Among the carbonate samples, LA-ICP-MS analysis of LAS20 shows the smallest errors, $\sim 5\%$ for minor elements and 5–10% for trace elements. Therefore, we selected LAS20 as a standard for foraminifera measurements.

Table 3 lists the $^{26}\text{Mg}/^{43}\text{Ca}$, $^{88}\text{Sr}/^{43}\text{Ca}$, $^{138}\text{Ba}/^{43}\text{Ca}$ and $^{238}\text{U}^{16}\text{O}_2/^{43}\text{Ca}$ ratios of four natural calcium carbonate samples measured by Nano-SIMS. Analysis spots with 5–6 μm diameter were selected on the surface of the samples so as to avoid those already measured by LA-ICP-MS. The errors are one sigma, estimated by the reproducibility of 10–20 spot measurements as well as those of a standard sample (JDo-1)

Table 3 Minor and trace elements in calcium carbonate samples measured by Nano-SIMS

Sample	$^{26}\text{Mg}^+ / ^{43}\text{Ca}^+ (\times 1)$	$^{88}\text{Sr}^+ / ^{43}\text{Ca}^+ (\times 1)$	$^{138}\text{Ba}^+ / ^{43}\text{Ca}^+ (\times 0.01)$	$^{238}\text{U}^{16}\text{O}_2^+ / ^{43}\text{Ca}^+ (\times 0.01)$	Corrected $^{138}\text{Ba} / ^{43}\text{Ca} (\times 0.01)$
LAS20	0.980 ± 0.051	0.679 ± 0.033	1.030 ± 0.107	0.726 ± 0.097	0.834
NBS19	0.463 ± 0.021	0.264 ± 0.012	0.220 ± 0.022	0.0019 ± 0.0008	0.127
TN2349	0.122 ± 0.012	0.131 ± 0.013	0.035 ± 0.003	0.121 ± 0.044	0.011
SPA4	0.100 ± 0.007	1.555 ± 0.112	0.660 ± 0.050	0.553 ± 0.151	0.640

Errors are one sigma.

Fig. 3 Comparisons between LA-ICP-MS and Nano-SIMS analysis of four natural calcium carbonates. They are Mg/Ca (3a), Sr/Ca (3b), Ba/Ca (3c) and U/Ca (3d). The U/Ca ratio of NBS19 is referred from solution analysis in Table 1. Errors are portrayed at the one-sigma level. Generally, Nano-SIMS data agree with those of LA-ICP-MS.

combined in quadrature. The precision is 5% – 10%, except for the $^{238}\text{U}^{16}\text{O}_2 / ^{43}\text{Ca}$ ratios. It is documented that Pb is emitted almost entirely as Pb^+ while formed $\text{UO}_2^+ : \text{UO}^+ : \text{U}^+$ are 10:10:1 on monazite $[(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4]$ sputtered by a $^{16}\text{O}^-$ primary beam of Nano-SIMS.¹⁵ In the present case, the formed $\text{UO}_2^+ : \text{UO}^+ : \text{U}^+$ in calcium carbonates are 50:7:1, which implies that metal ions of U are negligibly small. Therefore, we take the $^{238}\text{U}^{16}\text{O}_2 / ^{43}\text{Ca}$ ratios instead of the simple $^{238}\text{U} / ^{43}\text{Ca}$ ratios. We speculate that the relatively high UO_2^+ yield of LAS-20, compared with monazite,¹⁵ may reflect the 6+ oxidation state of U in LAS-20,²⁵ whereas U in monazite is likely to be present in the 4+ oxidation state.

Figure 3 shows a comparison between LA-ICP-MS and Nano-SIMS data of four natural carbonates. The U/Ca ratio of NBS19 is referred from the solution analysis in Table 1. The errors are portrayed at the one-sigma level. The Mg/Ca ratios measured by LA-ICP-MS agree well with those by Nano-SIMS within the experimental error margin (Fig. 3a). A linear-regression analysis of the data gave a slope of 0.03372 ± 0.00080 (1 sigma) and a Y-intercept of 0.0049 ± 0.0128 (1 sigma) with a correlation coefficient of $R = 0.9994$, which indicates that the data are analytically indistinguishable. The other minor element ratio, the Sr/Ca values, show a similar trend between LA-ICP-

MS and Nano-SIMS. A Y-intercept of 0.0201 ± 0.0328 (1 sigma) with $R = 0.9985$ implies that the best-fit correlation line would cross the origin of the coordinate axes (Fig. 3b). The Ba/Ca ratios measured by LA-ICP-MS are comparable with the Nano-SIMS data. However, the Y-intercept of 0.000642 ± 0.000331 (1 sigma) means that the line barely goes through the coordinate origin (Fig. 3c). The other trace element ratio, the U/Ca values of LA-ICP-MS are generally consistent with those of Nano-SIMS, even though the experimental errors are relatively large (Fig. 3d). Again, the Y-intercept of 0.000257 ± 0.000360 (1 sigma) shows that both data sets are in agreement. These lines of evidence suggest that the Nano-SIMS measurements at a spot size of 5 – 6 μm are mostly reliable and accurate with 5% – 10% precision, except for the trace element ratios, even though we should take into account the sample homogeneity.

Secondary-ion yields

Generally, secondary ion yields are required to convert the observed peak intensities into concentrations of elements by using SIMS. If matrix effects are significant, a good matrix-matched calibration standard is required. It is well documented that the sensitivity for Al relative to Si differs appreciably in different silicate mineral samples.²⁶ There are quite large variations in the secondary ion yields of major elements in olivines and low-Ca pyroxenes.²⁷ In order to explain the matrix effect, a bond-breaking model was proposed for the ionization process,²⁸ even though the model cannot predict the effect for complex samples quantitatively. Therefore, it is fully accepted that quantitative SIMS analysis requires good calibration standards with approximately similar major chemistry to the samples being analyzed.

We calculated the secondary ion yields of Mg, Sr, Ba and UO_2 relative to Ca based on the observed ratios (Table 3) and those determined by LA-ICP-MS (Table 2). Table 4 lists the secondary ion yields in NIST standard silicate glasses (SRM610 and 612) and natural calcium carbonate samples (LAS20, NBS19, TN2349 and SPA4). Simple averages are also added in the lower line. Generally, the relative secondary ion yields do not vary within a single matrix, such as silicate glass and calcium carbonate, while those of Mg/Ca and UO_2/Ca for calcium carbonate are significantly different from those for silicate glass (see average of Table 4). This is consistent with the idea that a good matrix-matched calibration standard is required for quantitative SIMS analysis.

A large variation is observed in the relative yields of Ba/Ca of different calcium carbonates, varying from 1.07 to 3.95 (Table 4). This may be attributable to an experimental artifact, and there may be isobaric molecular interference on ^{138}Ba . Note that the Ba isotopic composition of TN2349 did not agree with the reference value, as stated above. We carefully studied the mass spectra around 136 and 137, and finally found that the molecular ion Ca_2MgO_2 is a candidate of interference, since the ratio of $^{40}\text{Ca}_2^{24}\text{Mg}^{16}\text{O}_2$ (136 amu) to $^{40}\text{Ca}_2^{25}\text{Mg}^{16}\text{O}_2$ (137 amu) is

Table 4 Relative secondary ion yield of Mg, Sr, Ba and U in glass and calcium carbonate

	Mg/Ca	Sr/Ca	Ba/Ca	UO ₂ /Ca	Corrected Ba/Ca
Glass					
SRM610	0.76	1.86	1.77	0.068	—
SRM612	0.67	2.13	2.03	0.078	—
Average	0.72	2.00	1.90	0.073	—
Calcium carbonate					
LAS20	0.42	1.91	1.07	0.081	0.86
NBS19	0.40	2.45	2.04	0.074	1.18
TN2349	0.41	2.41	3.95	0.114	1.22
SPA4	0.52	2.05	1.08	0.096	1.04
Average	0.44	2.21	2.03	0.092	1.08

similar to the $^{24}\text{Mg}/^{25}\text{Mg}$ ratio. Secondary ions of $^{138}\text{Ba}^+$ and $^{40}\text{Ca}_2^{26}\text{Mg}^{16}\text{O}_2^+$ can only be separated at a high mass resolution of 18000. This is well beyond the possibility of Nano-SIMS, if a useful sensitivity is to be maintained. Therefore, we corrected the interference of $^{40}\text{Ca}_2^{26}\text{Mg}^{16}\text{O}_2^+$ on $^{138}\text{Ba}^+$ based on the empirical relationship that the $^{40}\text{Ca}_2^{24}\text{Mg}^{16}\text{O}_2^+/^{24}\text{Mg}^+$ ratio equals 0.002 in a calcium carbonate matrix, as follows:

$$(^{138}\text{Ba}/^{43}\text{Ca})_{\text{cor}} = (^{138}\text{Ba}/^{43}\text{Ca})_{\text{obs}} - (^{26}\text{Mg}/^{43}\text{Ca})_{\text{obs}} \times 0.002, \quad (1)$$

where the subscripts “cor” and “obs” denote the corrected and observed ratios. The corrected $^{138}\text{Ba}/^{43}\text{Ca}$ ratios of calcium carbonate samples are listed in the right-most column of Table 3. Figure 3c shows the relationship between the corrected $^{138}\text{Ba}/^{43}\text{Ca}$ ratios and the ICP-MS data together with those of the original data. A linear-regression analysis of the corrected data gives a relatively smaller slope of 0.000467 ± 0.000043 (1 sigma) and Y-intercept of 0.000307 ± 0.000402 (1 sigma). The Y-intercept is two-times smaller than that of the original value, suggesting that the correction works well. The corrected secondary ion yields of Ba/Ca based on the Eq. (1) are listed in the rightmost column of Table 4. Note that the variation is significantly reduced when compared with the original uncorrected values.

No systematic relationship appears to exist between the secondary ion yields (Table 4) and the physical characteristics of Group II elements (Mg, Ca, Sr, and Ba), such as the ionic radius and electronegativity. Based on the local thermal equilibrium (LTE) model²⁹ as applied to secondary ion production by $^{16}\text{O}^-$ ion bombardment, the following equation³⁰ is derived:

$$n_{\text{M}^+}/n_{\text{M}} = \text{const} \times (T^{3/2}/n_{\text{e}^-}) \times (B_{\text{M}^+}/B_{\text{M}}) \times \exp(-I_{\text{M}}/kT), \quad (2)$$

where T is the plasma temperature in K, n is the number of atoms, ions and electrons, B is the partition function of the atoms or ions and I_{M} is the ionisation potential. If this is applicable to the present case, the relative secondary ion yields of Group II elements are probably functions of the ionization potential as follows:

$$S_{\text{A}}/S_{\text{Ca}} = \text{const} \times \exp\{(I_{\text{Ca}} - I_{\text{A}})/kT\}, \quad (3)$$

where S is the secondary ion yield of Group II elements indicated by the subscript ($\text{A} = \text{Mg}, \text{Sr}$ or Ba). Figure 4 shows the relationship between the secondary ion yields for Group II (normalized to Ca) in silicate glass and a calcium carbonate matrix and the first valence ionization potential. The relative

Fig. 4 Relationship between the secondary ion yields of Group II elements and the ionisation potential of the first valence. The thick line shows a trend expressed on the basis of Eq. (3).

Fig. 5 Composite image of foraminifera (*Globigerinoides sacculifer*) taken by EMP. This sample was assigned by F1-4 in Table 5, together with approximate position of analyzed spots (1-4) by Nano-SIMS.

secondary ion yields decrease with increasing ionization potential, even though the data are somewhat scattered. The trend illustrated by the thick line in Fig. 4 is consistent with the correlation expressed by the basis of Eq. (3). Even though the chemical compositions of silicate glasses are appreciably different from calcium carbonate, the decreasing trend with the ionization potential is similar. There may be some physical mechanism, such as the LTE model,²⁹ which can explain the relationship observed in Fig. 4, irrespective of the chemical compositions (matrix effect).

Foraminifera

The basis for the Mg/Ca paleothermometry method lies in laboratory experiments, showing that the partition coefficient of Mg^{2+} into inorganic calcite correlates strongly with temperature.⁵ A culture study³¹ of the temperature-dependent uptake of Mg in marine biogenic calcite has confirmed this issue. The Mg/Ca ratios of planktonic foraminifera have been used to estimate Quaternary sea surface temperatures.³² Thus, there has been increasing interest in using foraminifera Mg/Ca as a proxy for this temperature, and an inter-laboratory

Table 5 Minor and trace elements in foraminifera shells measured by Nano-SIMS

Foraminifera (G.-sac.)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (μ mol/mol)	U/Ca (μ mol/mol)
F1-1-1	3.76	1.13	16.0	0.187
F1-2-1	2.79	1.14	5.77	0.251
F1-3-1	2.79	1.20	5.31	0.398
F1-4-1	3.56	1.11	10.7	0.156
F1-4-2	3.02	1.11	8.49	0.329
F1-4-3	5.30	1.03	10.8	0.202
F1-4-4	2.16	1.19	7.16	0.500
Average	3.34	1.13	9.18	0.289
STDEV	1.01	0.06	3.70	0.126

calibration was recently carried out.³³ Note that all of these experiments were undertaken by bulk analysis.

The $^{26}\text{Mg}/^{43}\text{Ca}$, $^{88}\text{Sr}/^{43}\text{Ca}$, $^{138}\text{Ba}/^{43}\text{Ca}$ and $^{238}\text{U}/^{43}\text{Ca}$ ratios of four shells of foraminifera (*Globigerinoides sacculifer*) were measured by using Nano-SIMS at spot sizes of 5–6 μm . Data were calibrated against those of LAS20 on the same mount. Four spot analyses were carried out on the F1-4 sample (Fig. 5), while only one spot was analyzed on the other samples. During the measurements, we selected inclusion-free and crack-free homogeneous regions. Table 5 lists the observed Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios of the foraminifera. The precisions were estimated by the reproducibility of repeated spot analysis of LAS20, ~5% for minor elements (Mg and Sr) and ~10% for trace elements (Ba and U) at one sigma, since the error of a single spot analysis on the actual sample (estimated by the standard deviation of 50 ratios set) is smaller than those of the standard with multiple spot analyses.

The Mg/Ca ratios vary significantly from 2.16 to 5.30 mmol/mol, which is much larger than the analytical precision. Even in a single shell (F1-4), the variation is up to $\pm 38\%$, which corresponds to a temperature variation of $\pm 4-5^\circ\text{C}$, based on a recently published calibration equation:³⁴ $\text{Mg/Ca} = 0.38 \times \exp(0.090T)$, where T is the seawater temperature in $^\circ\text{C}$. On the other hand, when we take the average of all data, the mean value of 3.34 agrees with the Mg/Ca ratio of 3.15 obtained by a conventional method on bulk basis (Sagawa, personal communication). The estimated temperatures by $\text{Mg/Ca} = 3.34$ and/or 3.15 agree with the field observation. This may indicate that although the Mg/Ca ratio is useful as a paleoceanographic proxy on the bulk scale, it may reflect more complex patterns at $<10 \mu\text{m}$ scale, such as a biological control revealed in coral skeletons.¹⁴ In contrast, the Sr/Ca ratios are rather constant, which may be related to the fact that the glacial-interglacial variation of planktonic foraminifera Mg/Ca is typically on the order of 20–25%, while that of Sr/Ca is only 5–6%.³³ The mean value of all Sr/Ca measurements, 1.13 (see Table 5), is again consistent with the bulk Sr/Ca ratio of 1.08 (Sagawa, personal communication). The variations of trace elements (Ba/Ca and U/Ca) are at the same level as that of the Mg/Ca ratios. There is a slight negative correlation between Mg/Ca and U/Ca ($R = 0.710$), which may also be attributable to a temperature effect. However, the details are beyond the scope of this paper.

In conclusion, an analytical procedure for minor elements (Mg and Sr) and trace elements (Ba and U) in natural calcium carbonates has been developed using a high lateral resolution secondary ion mass spectrometer (Nano-SIMS NS50) installed

at the Ocean Research Institute, the University of Tokyo. The probe diameter is significantly smaller than that available using comparable microanalysis methods, set at 5–6 μm on the sample surface, yet the detection limit is less than 1 $\mu\text{mol/mol}$. The observed Mg/Ca, Sr/Ca, Ba/Ca and U/Ca ratios of carbonate samples measured by Nano-SIMS agree with those measured by LA-ICP-MS using a larger probe, confirming their reported precision and accuracy. Foraminifera shells were analyzed by Nano-SIMS, and the averages of the Mg/Ca and Sr/Ca ratios are consistent with data obtained by a conventional bulk-analysis method. This procedure may be applicable to a wide range of earth and environmental studies, since the elemental ratios of biogenic carbonates provide possible paleoclimate proxies, and more generally are good indicators of the geochemical reaction and transport in many geological environments.

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