Determination of low B/Ca ratios in carbonates using ICP-QQQ

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Abstract

The very low B/Ca ratios characteristic of some natural biogenic carbonates, are of interest for research in ocean acidification but represent an analytical challenge. We describe a method using a novel instrument configuration (ICP-QQQ), for which we are not aware of any previously published geological applications, and for coccoliths, a sample type unique in its low B content and organic phases. Detection limits as low as 0.41 μmol/mol were achieved. Isobaric interferences, out of the reach even for SF-ICP-MS, can be solved using this instrument, which permits the safe measurement of the lowest abundance Ca isotope (46Ca). This allows maximizing the B concentration measured (matrix concentration up to 800 ppm Ca) while maintaining both B and Ca signals in counting mode. More significantly for low B samples, the ICP-QQQ is also able to overcome the interference of the ubiquitous 12C tail on the 11B mass, which otherwise leads to significant overestimates at very low B concentrations. This could be a reason for the significantly lower B/Ca ratios observed for the low B content interlaboratory calibration standards (Carrara and OKA), leads also to B/Ca overestimates due to porosity effects, as previously observed using LA-ICP-MS. This approach also permits the interference-free measurement of P/Ca and S/Ca ratios, which could be used as indicators of the complete removal of the organic matter from the samples.

1. Introduction

Biogenic calcite (CaCO3) is formed in the surface and deep ocean by a variety of organisms. The elemental and isotopic composition of this CaCO3, accumulating perpetually on the seafloor, is widely used to reconstruct seawater chemistry and environmental conditions in the oceans in the past.

Recently, interest has emerged in measuring B/Ca ratios in biogenic carbonates as an indicator of seawater or biomineralization pH, and carbonate ion concentration in the case of foraminifera. This is because the pK for borate to boric acid equilibrium is close to the natural pH range in seawater, and the incorporation of borate but not boric acid in the mineral structure makes its B content rise with increasing pH [Sanyal et al., 2000]. In the CaCO3 produced by planktic foraminifera, extracted from marine sediments, B/Ca ratios in the range of 50–200 μmol/mol have been determined [Ni et al., 2007, Yu et al., 2007; Foster, 2008]. Analysis by quadrupole ICP-MS [Yu et al., 2007] of solutions at 100 ppm Ca report detection limits of 10 μmol/mol. Analysis by sector field (SF) ICP-MS of solutions at 1 mM Ca report similar precision of B/Ca (3%, 2σ) in this concentration range but do not report detection limits [Ni et al., 2007]. Recent methods, also with a modern SF-ICP-MS have enabled determinations of B/Ca ratios in the range of 9–200 μmol/mol, using low amounts of CaCO3 (5 μg) at 10 ppm Ca with detection limits at the 2 μmol/mol level [Misra et al., 2014].

Measurement of B/Ca in biogenic carbonate produced by marine algae of class coccolithophorids is also of interest since this group of organisms is potentially jeopardized by ocean acidification [Doney et al., 2009]. If a lowered biomineralization pH contributes to the observed reduction of calcification at low seawater pH, this might be reflected in the B/Ca ratio in the calcite plates or coccoliths of this organism. However, this objective is significantly more analytically challenging than that of foraminifera. The first determinations of B/Ca in coccoliths via SIMS of the solid carbonate suggested B contents as low as 5 μmol/mol [Stoll et al., 2012a], well below the reported detection limits of most published solution-based...
measurements [Yu et al., 2007] so far and close to the lowest one [Misra et al., 2014]. Due to the low concentrations and porosity effects of the samples, SIMS B determinations may be curtailed by low analytical precision and poor reproducibility [Stoll et al., 2012a; Mejia et al., 2013]. Here we describe a new solution-based analytical method using ICP-QQQ Agilent 8800 (Tokyo, Japan) to permit improved accuracy and reproducibility for measurement of the very low B/Ca ratios in coccoliths produced in laboratory cell cultures. In addition to the low B content, such sample types are also potentially challenging because the culture material is much richer in elements derived from organic cellular phases, like N, S, and P, compared to biogenic carbonates like foraminifera extracted from sediments employed in most in previous studies [Yu et al., 2007; Foster, 2008; Yu et al., 2005] where microbial activity has very effectively eliminated organic contributions. Such elements may give rise to a broader range of polyatomic interferences in ICP-MS analysis. Our approach here uses the ICP-QQQ instrument to correct for potential polyatomic and isobaric interferences on the very low abundance $^{46}$Ca isotope. This in turn allows maximizing the solution concentration, and thus the target B counts, without $^{46}$Ca entering in analog detection mode. In addition, the extremely high abundance sensitivity of the ICP-QQQ turns out to be critical for removing the interference of the $^{12}$C tail, coming from the high amounts of carbonate present, on $^{11}$B measurements, typically observed in Quadrupole-based and even SF-based instruments [Heumann et al., 1998]. Finally, we report measurements of P/Ca and S/Ca on these samples, using recently published analytical methods [Diez et al., 2012], as incorporation of P in calcite may also be pH dependent [Stoll et al., 2012b] or indicative of the amounts of organic matter persisting the sample after external oxidative cleaning.

2. Materials and Methods

2.1. Instrumentation

All analyses were conducted by an ICP-QQQ (Agilent 8800, Tokyo, Japan) in the MS/MS mode. The instrument configuration consists of two quadrupole mass filters (Q1 and Q2) with a collision/reaction cell between them, which offers multiple approaches for chemical resolution based on selective reactions between ions selected by Q1 and the molecules of the gas present in the cell. In the first selectivity level, targeted analyte ions with the corresponding isobaric and/or polyatomic interferences are selected in Q1, which works as a 1 amu window band-pass mass filter. Subsequent chemical resolution can then be achieved in two ways. First, the interferences can be shifted to new product ion masses after reaction with the cell gas, while analyte ions stay at the same mass. Then, interference-free detection of the analyte can be achieved by setting Q1 and Q2 at the same m/z (on mass mode). We employ this approach here to remove isobaric (Ti) and polyatomic interferences on the extremely low abundant $^{46}$Ca. An alternative approach can be used for the case where the analytes react with the gas more effectively than their interferences, by setting the second quadrupole (Q2) at the corresponding higher m/z, depending on the adduct formed (mass shift mode). We employ this approach to detect trace amounts of the highly interfered P and S [Diez et al., 2012]. The ICP-QQQ configuration enabling interference-free detection of Ca and S and P is given in supporting information Figure S1.

For all measurements here, the instrument was operated in MS/MS mode using O$_2$ as reaction gas in the cell (see supporting information Table S1) The sample introduction system utilized during the experiments was a PFA Inert Sample Introduction Kit (Agilent, Waldbronn, Germany) integrated by a spray chamber and a connector tube, made both of PFA, and an inert torch with a 2.5 mm i.d. sapphire injector. The nebulizer was a PFA X-Flow (Savillex, Minnesota, USA) operated in self-aspiration mode (carrier flow of 1.0 L Ar min$^{-1}$), with makeup (0.1 L Ar min$^{-1}$) gas port and a 100 μL uptake line.

2.2. Samples and Standards

Solutions and standards were prepared from MilliQ grade water and ultrapure Teflon-subboiling 16 N HNO$_3$. All containers used for sample handling were leached in 3 N HCl with ultrasonication for 12 h and rinsed thoroughly (five times) with MilliQ before air drying in class 1000 clean lab. Primary standards (10,000 ppm for Ca and 1000 ppm B), were used to prepare synthetic standards with variable B/Ca and Ca concentration to cover the range of sample compositions. B contribution of the Ca standard was accounted for in standard additions. Standards and samples were prepared in a class 1000 cleanroom. To evaluate instrumental efficiency for eliminating polyatomic interferences, standards of Ca with Ti, and combinations
of N, P, and S were also prepared (from primary CPI Peak Performance ICP grade standards for Ti and N, and Merck ICP standards for P and S).

Treatment of culture samples follows that of Stoll et al. (2012a). Briefly, cells from culture were collected on 0.8 µm pore polycarbonate filters, rinsed with distilled water, and dried. Subsequently, material was resuspended from the filter in solution of hydroxylamine HCl to reduce Fe oxides that may form on cell surfaces. Following six rinsing steps in MilliQ, samples were subjected to three hot oxidation steps to minimize the abundance of organic matter in the remaining CaCO₃ concentrate. Cleaned culture CaCO₃ was weighed into cleaned eppendorf tubes and dissolved by addition of sufficient 0.1 N HNO₃. This acid strength, slightly weaker than other studies [Hathorne et al., 2013] was selected to further minimize contribution from any remaining organic matter present in culture samples. Natural carbonates from previous laboratory intercalibration studies were dissolved by addition of sufficient 0.1 N HNO₃. To yield 800 ppm Ca solutions, 400–600 µg CaCO₃ was dissolved in volumes from 200 to 300 µL. Further details on culture growth are given in supporting information Table S2.

2.3. Methodology
2.3.1. Cleaning Procedure
In order to minimize the sample consumption and achieve the lowest signal noise, the nebulizer was operated in self-aspiration mode at 100 µL/min. A 10% ammonia cleaning solution between samples was employed to minimize B carry-over. In order to avoid acid-base reaction between samples and ammonia, milliQ water was also introduced in the system after and before each sample. In this way, the total wash time between samples was 1 min. Sample consumption was 200 µL. The analytical sessions were reduced to 3–4 h in order to avoid any possible sample deposit over the ICP cones.

2.3.2. Mass Spectrometry
Elemental detection was carried out with an ICP-QQQ. Oxygen was introduced in the collision/reaction cell at a flow rate of 0.30 mL min⁻¹. Operation conditions are shown in supporting information Table S1. S, P, and Ti were detected in mass shift mode as their corresponding oxides (SO, PO, and TiO) after their reaction with oxygen in the cell. In contrast, Ca and B, which do not react with oxygen in such conditions, were measured in on-mass MS/MS mode. Transitions for all analytes measured are also shown in supporting information Table S1. The integration time for each of the targeted isotopes was 150 ms and only one point per mass peak was selected for each isotope. ⁴⁶Ca and ¹¹B isotopes were monitored during the coccolith samples and standards analysis in the calibration plot (five replicates for each calibration point). Total analysis time, including stabilization time, was 2 min. Optimum conditions for P and S measurement are described elsewhere [Diez et al., 2012].

3. Results and Discussion
3.1. Spectral Interferences Over ⁴⁶Ca
It is well known that precision for multielemental ratios can be significantly improved if signals from both elements are collected in the same mode [Marchitto, 2006; Rosenthal et al., 1999]. Since B is an ultratrace element in our coccolith samples (around 5 µmol/mol) [Stoll et al., 2012a], both elements had to be measured in counting mode. For that purpose we chose the least abundant Ca isotope, ⁴⁶Ca (0.004%) that allowed us to increase the B concentration and the corresponding matrix concentrations (up to 800 ppm Ca) in the measured solutions, without going to analog mode. Of course, this approach requires that there is no isobaric interference of ⁴⁶Ti over ⁴⁶Ca. Some natural biogenic carbonates (foraminifera) have exhibited sufficient Ti concentration to bias ⁴⁶Ca measurements in SF-ICP-MS [Marchitto, 2006]. The resolution power required to physically separate the ⁴⁶Ti and ⁴⁶Ca mass peaks (~43,000) is not achievable with any commercial ICP-MS instrument. However, on the ICP-QQQ instrument, the different reaction enthalpies of Ca⁺ and Ti⁺ with O₂ in the reaction cell (+1.53 eV and −1.63 eV, respectively) [Agilent, 2012] can be used to chemically resolve such isobaric interference. The first quadrupole located between the ion lenses and the reaction cell allows selecting the analyte and its on-mass interferences at mass 46 among all the ions present in the sample. Then, ⁴⁶Ti reacts completely with the O₂ present in the cell forming TiO⁺ (m/z = 64), while ⁴⁶Ca does not react at all, and thus maintains its original m/z at 46 [Balcaen et al., 2014]. Finally, the second quadrupole after the reaction cell selects the ⁴⁶Ca isotope and filters out the new formed ⁶²TiO allowing an interference-free detection. In comparison to standard Quadrupole-based instruments equipped with a simple reaction cell, the presence of a first
quadrupole just after the ion lenses in the new ICP-QQQ (see supporting information Figure S1) allows to isolate the target m/z (m/z = 46 in the case of Ca) before entering the reaction cell, which makes its subsequent reaction with O₂ more specific, reproducible and matrix independent.

In order to check the efficiency of the isobaric interference removal, a synthetic standard containing 5 ppm of Ca and 0.01 ppm of Ti was measured in Single Quad mode, where the first quadrupole operates as an ion guide and therefore the instrument behaves as a standard quadrupole ICP-MS. As can be seen in Figure 1a, both isotopic patterns for Ca and Ti are clearly overlapped. The signal detected for ⁴⁶Ca is much higher than expected, which clearly indicates the positive interference from ⁴⁶Ti. In fact, the ⁴⁶Ca/⁴³Ca isotope ratio measured (0.0718 ± 0.0005) is far from the theoretical one (0.030 ± 0.022) [Berglund and Wieser, 2011]. However, when operating the instrument in MS/MS mode, Ti isotopes react completely with O₂, shifting the full Ti isotopic pattern to detection as oxides (m/z from 62 to 66; Figure 1b). Under such experimental conditions, the measured ⁴⁶Ca/⁴³Ca isotope ratio (0.0288 ± 0.0006) is in agreement with the theoretical one. The negligible signals of Ti peaks at m/z = 47, 48, and 50 confirms the complete reaction of Ti with O₂ (Figure 1b).

Considering the significance of organic phases on the samples, the influence of polyatomic interferences from N, S, and P on ⁴⁶Ca (¹²C³⁴S, ³²S¹⁴N, ¹⁶O₂¹⁴N, ³¹P¹⁵N) cannot be ruled out. In fact, ¹⁴N¹⁶O₂ interference has been previously described in SF-ICP-MS techniques for biogenic marine carbonates [Marchitto, 2006]. The use of MS/MS mode with reacting O₂ molecules in the reaction cell of the ICP-QQQ should remove completely such polyatomic interferences. In order to demonstrate this, we measured the ⁴³Ca/⁴⁶Ca isotope ratio in several
3.2. Spectral Interferences Over $^{11}$B

The on mass mode was used for B detection because the reaction yield of B$^+$ with O$_2$ present in the reaction cell is very low (reaction enthalpy $+1.39$ eV). Surprisingly, it was found that the most significant interference on the B/Ca ratio was the tail of $^{12}$C over $^{11}$B, mainly due to the very low abundance of B in the samples studied and the large amounts of C present in our highly concentrated CaCO$_3$-rich matrix. The abundance sensitivity problem, describing the contribution of the peak “tail” of a major isotope (with a certain m/z value) to an adjacent m/z value [Murray et al., 2013; Becker, 2007], is greatest in single quadrupole configurations (2 $\times$ 10$^{-6}$) [Boulyga and Becker, 2002]. Indeed, the contribution of the $^{12}$C tail over the $^{11}$B signal using Q-based ICP-MS has been previously reported [Heumann et al., 1998]. Although in samples of higher B concentrations (B/Ca 41–221 $\mu$mol/mol) there is no appreciable bias of B/Ca ratios [Yu et al., 2005], it may be significant in lower B samples, like the ones analyzed in this work. On the ICP-QQQ, the MS/MS operation of two mass analyzers yields unmatched abundance sensitivity ($<$10$^{-16}$) [Liba, 2013], orders of magnitude better than Sector Field instruments operated in low and medium resolution (5 $\times$ 10$^{-6}$ and 3 $\times$ 10$^{-7}$, respectively [Boulyga et al., 2006; Boulyga and Becker, 2002]. Additionally, part of the very abundant C reacts with the O$_2$ in the MS/MS mode, reducing the magnitude of the massive $^{12}$C peak.

To verify the resolution of the large $^{12}$C peak from the trace $^{11}$B signal, a solution of 0.5 ppb B in CaCO$_3$ matrix at two different concentration levels, 1.3 (Figure 2a) and 0.10 (Figure 2b) mg carbonate/mL was measured in single Q and MS/MS mode for comparison purposes. When measuring with standard abundance sensitivity, analogous to conventional quadrupole instruments, and high matrix concentration (840 ppm Ca, 2 $\mu$mol B/mol Ca) a significant tail from the massive $^{12}$C peak affects the $^{11}$B signal (Figure 2a) and results in poor precision and significantly biased $^{10}$B/$^{11}$B isotope ratio (0.095 ± 0.011) distinct from the theoretical value given by the IUPAC (0.248 ± 0.009) [Berglund and Wieser, 2011]. However, it is worth stressing that when the matrix content is not so high (67 ppm Ca) and the B/Ca is higher (28 $\mu$mol/mol), although the influence of the $^{12}$C tail is still clear (Figure 2b), it does not affect significantly the B isotopic pattern and therefore the B/Ca measurement.

In contrast, using the MS/MS mode, the two signals are fully isolated, and therefore $^{11}$B and the B/Ca ratio measured become completely independent of the carbonate concentration (Figures 2c and 2d). This is additionally proved by the precisely measured $^{10}$B/$^{11}$B isotope ratio (0.233 ± 0.009 and 0.233 ± 0.007, for high and low carbonate concentration levels respectively), which matched quite well with the theoretical value, even at the very low B level measured. In fact, the small difference between the theoretical and experimental B isotope ratio values is likely due to mass discrimination caused by preferential transmission of heavier ions ($^{11}$B in this case) from the ICP source to the detector. Mass discrimination factors ranging from −4.2 to 6.5% were obtained, which agree well with the typical values repeated in the literature for B [Meija et al., 2012; Aggarwal et al., 2003].

Finally, we evaluated the $^{12}$C-tail effect on low B/Ca ratios as measured in our carbonate samples. For that purpose, a calibration set ranging from 10 to 500 $\mu$mol B/mol Ca was analyzed using again both operating modes, Single Q and MS/MS. After plotting the experimental $^{11}$B/$^{40}$Ca ratio obtained against the theoretical $\mu$mol B/mol Ca, the linear regression parameters were obtained. Then, we measured two standards with very low B/Ca ratios, 3.0 and 4.6 $\mu$mol B/mol Ca, which corresponds to 0.7 and 1.0 ppb B, respectively, where we expected an important influence of the C tail. In order to attenuate the influence of this tail in single Q mode, we selected one point per mass peak instead of three points. In this way, the quantitative measurement was exclusively carried out at the peak center. As expected, the MS/MS mode provided accurate results, 3.0 ± 0.8 and 5.0 ± 0.2, while the Single Q mode provided 4.1 ± 0.3 and 5.6 ± 0.5, results significantly elevated (by +37 and +22%, respectively) above the theoretical values due to $^{12}$C tail. Consequently, the influence of the C-tail should be always evaluated to avoid overestimates at the very low B/Ca ratios. In addition, the significance of
the C tail could also be important in determinations of $^{11}$B/$^{10}$B ratios in carbonates, especially if these were done in situ (either by LA-ICPMS or SIMS) rather than with column chemistry to separate the B from the carbonate matrix and $^{12}$C peaks.

### 3.3. Matrix Induced Mass Discrimination

A natural marble sample analyzed at varying dilutions in the concentration range from 200 to 800 ppm Ca shows no systematic change in measured B/Ca ratio with concentration (mean $29.8 \pm 0.8$ μmol/mol; rsd 2.6%; supporting information Figure S2). This suggests the absence of significant matrix-induced mass discrimination. This is a much larger range in sample concentration than was actually used for measured culture samples.

### 3.4. Calibration and Comparison With Interlaboratory Comparison Materials

A calibration plot was produced by increasing molar concentrations of B/Ca standards from 5 to 500 μmol/mol. Results are plotted in supporting information Figure S3. The calibration curve was linear along the concentration interval assayed ($R^2 > 0.999$). Internal precision was 4.2% (2σ) for 116 μmol B/mol Ca (medium point). Our B/Ca blank was 2.0 ± 0.3 μmol/mol (2σ). This absolute blank value is in agreement with that recently published using SF-ICP-MS (2.0 ± 1.0 μmol/mol) [Misra et al., 2014]. However, the precision associated to our blank was significantly lower likely due to the high quality reagents used and a more consistent measurement (instrumental stability). Interestingly, the ICP-QQQ used here allowed us to measure the $^{46}$Ca isotope and therefore both elements, B and Ca, could be detected in counting mode, which improves ratio precision significantly. This fact together with the complete interference-free detection (isobaric, polyatomics and C tail) while still using high matrix (and therefore B) concentrations could be the reason for our lower detection limits. In fact, we report a B/Ca detection limit as low as 0.41 μmol/mol (3σ of the blank), which implies a B/Ca quantification limit around 1.2 μmol/mol.

Calibration using the synthetic B/Ca solution yielded results for high B interlaboratory calibration standards JCT and JCP within the range of the reported values [Hathorne et al., 2013] (see Table 1). For these standards showing high B/Ca ratios similar values were obtained using analysis with the $^{11}$B/$^{43}$Ca ratio, suggesting effective suppression of interferences on $^{46}$Ca. Interestingly, the value obtained for JCP is also in good agreement with the value previously reported using ICP-MS, 459 ± 14 (2σ) [Dissard et al., 2012].

However for the low B interlaboratory standards OKA and Carrara Marble, our values here are considerably lower than those reported previously by isotope dilution using TIMS [Stoll et al., 2012a] as can be seen in...
Table 1. Quantification Values for the Interlaboratory Calibration Standards (OKA, CARRARA, JCT, and JCP)

| Interlaboratory Standard | Reference Value | Experimental Value ICP-QQQ |
|--------------------------|-----------------|----------------------------|
| CARRARA                  | 2.78            | 0.78 ± 0.19                |
| CARRARA (second day)     | 2.95            | 0.75 ± 0.23                |
| OKA                      | 6.16            | 2.64 ± 0.49                |
| OKA (second day)         | 6.23            | 2.39 ± 0.37                |
| JCT                      | 193             | 188 ± 10                   |
| JCP                      | 465             | 434 ± 11                   |

Table 1. Although our value for Carrara in two different analytical sessions (0.78 and 0.75 µmol/mol) is slightly below our estimated limit of quantification (therefore being of lower precision than the other determinations) it provides nonetheless significantly lower B/Ca ratio than the previously reported TIMS value. One interpretation is that TIMS isotope dilution determinations overestimated the B content due to the potential contribution of B blank and perhaps, to the incomplete isolation of the $^{11}$B signal from the $^{12}$C tail. If the values presented here are accurate, then B determinations previously made with OKA and Carrara as calibration standards will require revision [Stoll et al., 2012a].

3.5. B/Ca Ratios in Coccoliths Grown in a Laboratory Culture

We measured a series of five new coccolith samples grown in culture, along with eight samples which had been previously analyzed via SIMS. The B/Ca ratios measured by ICP-QQQ ranged from 3.7 to 28.0 µmol/mol (see Table 2).

Of the samples analyzed by both techniques, the average B/Ca of the SIMS analyzed samples (23.1) was higher by a factor of two compared to the ICP-QQQ measurement (10.0). In all but one sample, B/Ca was significantly lower when the ICP-QQQ was used for measurement. There was no significant correlation between the SIMS and ICP-QQQ determinations. Given the verified resolution of interferences and peak tailing avoidance on ICP-QQQ, we place higher confidence in the ICP-QQQ determinations. The higher average B content of coccoliths determined by SIMS is too large in magnitude to arise exclusively from $^{12}$C tail on $^{11}$B (abundance on ICP-QQQ, we place higher confidence in the ICP-QQQ determinations. The higher average B content of the SIMS and ICP-QQQ determinations. Given the verified resolution of interferences and peak tailing avoidance on ICP-QQQ, we place higher confidence in the ICP-QQQ determinations. The higher average B content of coccoliths determined by SIMS is too large in magnitude to arise exclusively from $^{12}$C tail on $^{11}$B (abundance sensitivity effects). It reflects in part the overestimate of the concentrations of B in the OKA and Carrara calibration standards. More importantly, we suggest that porosity effects of coccolith samples mounted for SIMS in Indium may have led to overestimates of B concentration in some cases. Samples of crushed NIST glass standards and diatom frustules with low B content (<2 ppm) yielded higher B intensities via SIMS when mounted in indium, with high porosity, than when mounted with no porosity in epoxy resin. Conversely, LA-ICPMS measurements on the same epoxy-mounted standards and samples confirm the B content measured via SIMS in the low porosity, epoxy mounted samples [Mejia et al., 2013]. The SIMS B determinations on coccolith samples, which were all made on indium-mounted material, may have suffered similar overestimates of B content. Only two coccolith samples, NSY 1300 and NSY 180, yielded higher B/Ca via ICP-QQQ than SIMS. This low-califying coccolith strain has a thinner coccolith morphology and may have been characterized by different porosity or beam-sample interaction during SIMS analyses than the more heavily calcified strains BP91 or EH2.

3.6. P/Ca and S/Ca Ratios in Coccoliths Grown in a Laboratory Culture

Finally, the use of ICP-QQQ also opened the door to the highly sensitive and specific measurement of two elements, P and S, which has been traditionally hampered so far using established Q and even SF-based ICPMS. These elements can provide useful and complementary
information since incorporation of P in calcite may be pH dependent [Stoll et al., 2012b] and both elements can be used as indicators of the successful removal of the organic matter from the sample after cleaning. Interestingly, the O2 used in the reaction cell for the removal of the isobaric and polyatomic interferences on 46Ca and 11B were also ideal for the free of interference measurement of P and S as their corresponding oxides [Diez et al., 2012].

Among the entire sample set, our P/Ca values ranged from 0.16 to 22.4 mmol/mol whereas S/Ca values varied by much less, from 0.63 to 1.51 (see Table 2). The three samples with highest P/Ca ratios all had B/Ca values which fell in the top quartile; overall a strong positive correlation between P/Ca and B/Ca is observed (r = 0.64, p < 0.02). Among the samples with P/Ca below 5 mmol/mol, a weak and marginally significant (r = 0.44, p = 0.21) positive correlation is present. The P and S may originate from organic phases in these samples, and the observed correlation with B may indicate a contribution of B from organic sources as well. A pH dependence on P partitioning in calcite, for example based on the HPO42-/CO32- ratio [e.g., Stoll et al., 2012b] would lead to an inverse correlation between B/Ca rather than the positive relationship observed here. P and S may derive from organic components trapped within the coccolith mineral, which are involved in the biomineralization [Henriksen et al., 2004], and which may be fully or partially solubilized upon dissolution of the coccolith calcite. Alternatively, P and S may be present in extracoccolith organic matter and either refractory to cleaning methods, or incorporated on the surface of the calcite during cleaning. Due to the thin size of coccoliths and their high solubility it is not possible to complete a weak acid etching as a final cleaning step as is routinely conducted with foraminifera. In either case, the relationship between organic phases and B in coccoliths may need to be further resolved in order to achieve reliable interpretations of B/Ca or 11B/10B data from natural samples.

In the data set of low to moderate P concentrations (≤5 mol/mol), for species E. huxleyi which has several replicates, no strong correlations were apparent between coccolith B/Ca and cell parameters. B/Ca shows the greatest correlation with growth rate and with calcification rate, the latter suggested in earlier work [Stoll et al., 2012a], yet neither relationship shows strong statistical significance (Figure 3 and Table 2; r = 0.41 p = 0.36, r = 0.42 p = 0.34, respectively). Calcification per cell, cellular carbon quota, and inorganic to organic calcite ratio of cells all show negligible correlation to B/Ca. The strong correlation between coccolith B/Ca and calcification rate observed in previous (SIMS) studies [Stoll et al., 2012a] may in part reflect analytical bias driven by different interactions of the beam with highly calcified coccoliths.

4. Conclusions

We report a method for determination of the low B/Ca ratios typical of coccoliths using the new ICP-QQQ instrument with the lowest detection limits reported to date for this analysis. We show that oxidatively
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aware, but the high abundance sensitivity and elimination of interferences may make the technique advantageous for determination of other trace elements of paleoceanographic interest in biogenic carbonate in the near future.
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