Reply to comments by S. K. Aggarwal and C.-F. You on "Determination of low B/Ca ratios in carbonates using ICP-QQQ"

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We appreciate the perspective offered by the authors [*Aggarwal and You*, 2016] on our paper. [*Diez Fernández et al.*, 2015]

Regarding the impact of the uncertainty in the relative abundance of the ^{46}Ca isotope, the authors suggest that the uncertainty has to be included on all the data presented in the paper. We clarify that such uncertainty does not apply to the reported B/Ca ratios. The reported B/Ca were quantified not using the relative abundances of each isotope but using a set of external calibration standards of known B/Ca ratio, as described in section 3.4 and illustrated in supporting information Figure S3. This is identical to the approach used in other studies of ratios of trace metals/Ca which have also employed ^{46}Ca (*Rosenthal et al.* [1999], *Yu et al.* [2005], and other publications based on these methods).

The uncertainty in the relative abundance of ^{46}Ca is relevant only in the method development (section 3.1) where we noted the Ca isotope ratios as a way to further confirm the shift of ^{46}Ti to ^{64}TiO in the QQQ method. The isotope ratio ^{46}Ca/^{43}Ca provides a direct confirmation using the target Ca isotope used in our B/Ca method (^{46}Ca, interfered by Ti) and a Ca isotope free of interference (^{43}Ca). However, the uncertainty of ^{46}Ca abundance in no way affects our conclusion that the interfering ^{46}Ti peak has been removed by our optimized experimental conditions. First, regardless of the uncertainty in the relative abundance of ^{46}Ca or the absolute correct value of ^{46}Ca/^{43}Ca abundance, the decrease by more than twofold in the ^{46}Ca/^{43}Ca ratio with the application of QQQ reaction (versus single quad) confirms unambiguously that the QQQ removes the Ti interference on mass 46. Figure 1 illustrates how the switch from single quad to QQQ shifts the Ti (via reaction with O$_2$) to TiO (m/z 63, 65, and 66) and shows the complete removal of the Ti interference over the Ca isotopes using QQQ with negligible signals obtained at m/z 47, 49, and 50 (where the corresponding Ti isotopes with abundances 7.44, 5.41, and 5.18% should be detected). In the second paragraph of this section, we compare the ^{46}Ca/^{43}Ca natural abundance ratio (0.030 $\pm$ 0.022, including the full uncertainty estimates as provided by the IUPAC [*Berglund and Wieser*, 2011]) with the ^{46}Ca/^{43}Ca measured in single quad and QQQ mode. The measurement in single quad mode yields a ^{46}Ca/^{43}Ca (0.0718 $\pm$ 0.0005) which falls outside the uncertainty estimates of the natural ^{46}Ca/^{43}Ca abundance, whereas after removal of Ti in QQQ, the measured ^{46}Ca/^{43}Ca (0.0288 $\pm$ 0.0006) overlaps with the natural abundance including uncertainty. The use of the ^{43}Ca/^{48}Ca isotope ratio, as suggested in the comment, could also demonstrate the removal of the interference but would be an indirect confirmation of our approach as it does not use our target ^{46}Ca isotope. The use of isotope ratios in our work was not an objective itself but, as mentioned above, just another perspective to further confirm our findings.

The QQQ technique produces values for high B carbonates (JCP and JCT) which are comparable to other techniques. Our JCT value is statistically undistinguishable from TIMS, 188 $\pm$ 10 and 193 μmol B/mol Ca, respectively. In the case of JCP, our value overlaps within error with the value previously reported (459 $\pm$ 14 μmol B/mol Ca, [*Dissard et al.*, 2012]) using a standard ICP-QMS-based procedure.

For low B carbonates, the QQQ yields B/Ca lower than either SIMS or TIMS, for different reasons in each case. For SIMS, an existing and already documented effect could explain this discrepancy. Previous study, focused on diatom B analysis[*Mejía et al.*, 2013], showed that SIMS does not yield correct B concentrations in the low B (NIST SRM 614) crushed standards when these are pressed in Indium (i.e., retain porosity), but can yield correct data when the same standard powders are mounted in epoxy resin (e.g., porosity is infilled). As this effect has been well documented with standards of known B content, we find it very

plausible that the same effect exists for powders of coccoliths mounted in indium in the reported SIMS study, as such samples would have retained porosity. Certainly in future work, LA-ICP MS or N-TIMS could be used to further check concentrations in coccoliths but LA-ICPMS would face the challenge of lower B concentrations than in the diatom studies in which it was employed previously.

For TIMS analysis of OKA and CARRARA, our understanding of the difference in values is limited in part by the absence of uncertainty estimates on the TIMS determinations for these. First, because we cannot verify whether our lower B/Ca measurements nonetheless fall within the uncertainty estimate of the TIMS determinations, we adopted a conservative language in our discussion (e.g., "perhaps," "our interpretation"). Second, we clearly indicated in the paper (top page 2011) that those samples were in the limit of our approach. In fact, Carrara values obtained in two different experimental sessions (0.78 ± 0.19 and 0.75 ± 0.23) were slightly below our estimated quantification limit (1.2 μmol B/mol Ca). Even the OKA values were also very close (2.64 ± 0.49 and 2.39 ± 0.37) to such quantification limit. Taken this into account, we gave our, as indicated above, conservative opinion in the paper (top of page 2011).

A further complication in addressing the differences between TIMS and QQQ analysis is the absence of information on the TIMS methodology and sample preparation for these particular TIMS analytical results. If the TIMS determinations were made in N-TIMS without chromatographic separation, the predominant interference, as the authors indicate, would not be the mass ^{12}C tail directly; however, other carbon-based interferences which would arise from the carbon-rich matrix are known (mostly CNO-combinations) [*Aggarwal and Palmer*, 1995] and could affect quantitative results. Alternatively, at the ultratrace levels of B for these materials, blank issues are a perpetual possibility [*Barth*, 1997], one which can augment with increasing sample processing steps prior to analysis.

Summarizing, it is evident that both Carrara and OKA B/Ca ratios are extremely low and it is difficult to obtain accurate and precise values for them using any analytical technique. In fact, such very low B/Ca ratios in biogenic carbonates have not been deeply studied so far. A lot of work in this field is expected and we think that the new ICP-QQQ approach proposed herein can play an important role. We agree that it would be of great interest to compare results for the same real samples analyzed simultaneously with different techniques such as ID-TIMS, ICP-QQQ, and SIMS or LA-ICPMS in order to identify the strong and weak points of the different approaches. Of course, this is out of the scope of this "proof of concept" paper but could provide a new challenge for future interlaboratory comparison studies.

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