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COMMENT

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Comment on "Determination of low B/Ca ratios in carbonates using ICP-QQQ" by S. D. Fernandez et al.

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This has comments on the paper entitled "*Determination of low B/Ca ratios in carbonates using ICP-QQQ.*" The authors present an interesting new development and have demonstrated the determination of low B/Ca amount ratios in carbonates in the μmol/mol range using Agilent ICP-QQQ in the MS/MS mode. It is an interesting piece of work with most of the problems of isobaric interferences, tail contribution etc. taken care by MS/MS mode in QQQ. However, we have a few observations on the data presented by the authors and would be happy if the authors' reply to the same.

The authors have used ^{46}Ca and ^{11}B to determine B/Ca ratio. As mentioned by authors, it is a nice idea to use low abundant Ca isotope so that both Ca and B can be measured in the ion counting mode, instead of measuring one isotope in the analog mode. ^{46}Ca is the lowest abundant isotope of Ca with its abundance as 0.004 atom%. However, there is also a very large uncertainty on its abundance. NIST data base [*Brand et al*., 2014] quotes an uncertainty of 75% on this abundance {atom fraction of ^{46}Ca = 0.00004(3)}. Thus, the data presented by authors by assuming atom % of ^{46}Ca as 0.004% must be given a relook and the large uncertainty of 75% on ^{46}Ca abundance has to be included in all the data presented in the paper. The authors can recalculate their data using ^{43}Ca (0.135 atom % with an uncertainty of 7.4%, abundance higher by a factor of about 34 compared to that of ^{46}Ca) and ^{48}Ca (0.187 atom % with an uncertainty of 11.2%, abundance higher by a factor of about 47 compared to that of ^{46}Ca), if these two isotopes were also measured using the ion counting detection mode. The authors measured ^{43}Ca/^{46}Ca isotope ratios, they could have also measured ^{43}Ca/^{48}Ca isotope amount ratios to enhance the confidence in the isotope ratio measurements.

The data presented by authors in Tables 1 and 2 show that B/Ca amount ratios obtained by them using ICP-QQQ are significantly lower compared to those reported previously using TIMS as well as SIMS. As mentioned by authors, the B/Ca ratios obtained by them for CARRARA and OKA samples are factors of 2-3 lower than those reported by TIMS. However, these are 2.6% and 7.1% lower for JCT and JCP samples, respectively. The B/Ca ratios in CARRARA ad OKA samples are low by two orders of magnitude compared to those in JCT and JCP. The authors state "one interpretation is that TIMS isotope dilution determinations overestimated the B content due to potential contribution of B blank and perhaps, to the incomplete isolation of the ^{11}B signal from the ^{12}C tail." First, there is no question of ^{12}C tail since in TIMS, B is not measured as B^+ ion but as an alkali metal borate ion and also one does not get C^+ ions in TIMS due to the fact that the first ionization potentials of both C and B are quite high. Of course, if the boron blank is not taken care of (which the labs. would have controlled and checked), then one cannot compare the data by any technique.

The data presented in Table 2 are a comparison of the results obtained using ICP-QQQ and those obtained by SIMS previously. Again the results of ICP-QQQ are significantly lower compared to those of SIMS, for 6 out of 8 samples, with factors of 1.6 to about 6. The authors agree that the higher values by SIMS cannot be explained due to the abundance sensitivity effects of ^{12}C tail. If these differences are due to sample-beam interaction effects in SIMS, data on at least a few samples can be checked by LA-ICPMS or preferably by ID-TIMS.

It is difficult to digest that the two independent techniques viz. isotope dilution TIMS as well as SIMS would give wrong (higher) results on different kinds of samples for B/Ca in carbonate samples.

It must be mentioned that the efforts by authors on measuring B/Ca amount ratios in these samples are worthy of high appreciation in view of the first published geological application of ICP-QQQ, but these results must be studied critically. The newly used technique of MS/MS in ICP-QQQ surely holds a great potential for determining trace elements of paleooceanographic interest in biogenic carbonates in future.

Reference

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