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Climate of the Past Discussions

Interactive comment on "Element/Calcium ratios in middle Eocene samples of <i>Oridorsalis umbonatus</i> from Ocean Drilling Program Site 1209" *by* C. F. Dawber and A. K. Tripati

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Author's comments on Anonymous review 1 and 2:

Reply to Anonymous Referee 1 comments:

Referee comment: "these authors apply their calibration and attempt to interpret the middle Eocene X/Ca variations observed in context of shifts in the carbon cycle. However as the authors themselves state the records are complicated and do not consistently show any similar trends either between the X/Ca records or with the carbon cycle proxies. This leaves the reader feeling dissatisfied"

and

Discussion – to re-iterate the authors really must provide some firmer conclusions at the moment the reader is left feeling uncertain about the impact and contribution that the dataset represents to the field. (e.g., lines 12-14)

Authors comment: It is routine for studies to explore the implications of a single element ratio proxy reconstruction for hydrography and assume a uni-variate or multi-variate core top calibration can be validly applied. In this manuscript, we set out test this assumption. Specifically we test the hypothesis previously presented to the community that element ratios in O. umbonatus can be used to reconstruct past variations in bottom water Δ[CO32-] (Lear et al. 2006; Lear and Rosenthal, 2010; Dawber and Tripati, Biogeoscience Discussions). We agree that one result is the finding that "records are complicated and do not consistently show any similar trends either between the X/Ca records or carbon cycle proxies." However, rather than use the same uni-variate or multi-variate approach to interpreting a single element ratio proxy and reconstruct Pacific intermediate water Δ[CO32-] for the early Paleogene (i.e., then potentially inaccurately interpreting our results in terms of the new information we can now discern about the coupling of the carbon cycle and global climate), we instead have chosen to take a new approach entirely.

We test coretop calibrations for multiple-proxies with these downcore data, with the aim of either producing paleoceanographic reconstructions of bottom water Δ[CO32-] that stand up to greater scientific rigor and evaluation, or demonstrating the starting assumptions are not robust. In this circumstance, the multi-proxy data did not support clear and consistent trends. Whilst Referee 1 may feel dissatisfied with this, we think this is an important cautionary message to populate throughout the community, which tends to interpret elemental proxies for carbonate system parameters in isolation, and one that was only possible to communicate using our thorough and multi-proxy approach.

Thus in this study, we are pushing element ratio proxies to the limit of our knowledge and in doing so, generating new questions and new avenues of investigation so that we might further our understanding of both proxy systematics and their limitations in paleo-oceanographic reconstructions. The only firm conclusion of our work is that the community must be cautious of paleo-bottom water Δ[CO32-] reconstructions based on foraminiferal element ratios and not overstretch the palaeoclimatic implications based on these reconstructions.

Referee comment: X/Ca-DCO3 calibration Dawber and Tripati cite their paper, currently in review, for the calibration equations to convert X/Ca into DCO3. The paper in review needs to be accepted or critically peer reviewed prior to the submission of this paper as the whole interpretation hinges on the calibration. Also the authors summarize available publications for O. umbonatus but fail to mention the work of Brown et al. 2011 (EPSL). Brown et al. 2011 thoroughly assesses the potential of B/Ca as a DCO3 proxy in similar a BWT and DCO3 range and determine that B/Ca in 0. umbonatus is insensitive to DCO3 changes. The authors need to address this in the manuscript.

Authors comment: We acknowledge that no reference is made to the Brown et al. (2011) paper, as at the time of our submission, the Brown et al. manuscript was not yet published. In light of the different conclusions reached by Brown et al. in contrast to our own regarding the suitability of O. umbonatus B/Ca as a sensitive proxy for bottom water Δ[CO32-] we would like to make the following comments on the possible origin of differences between the two studies.

Firstly, Brown et al. (2011) base their observations on a data set that consists of a limited number of core top measurements (n = 9). In contrast, the empirical relationships used in this study and those presented and discussed in Dawber & Tripati (BGD) are based on 37 core top measurements.

In addition, foraminiferal B/Ca is a notoriously difficult element ratio to measure in the lab with many potential sources of contamination arising both during sample prepara-

tion and analysis. We are confident in the O. umbonatus B/Ca ratios presented here as we have used the same laboratory facilities and followed the same procedure (Yu et al. 2005) that was developed at the University of Cambridge and that has been used in several previous studies that have been accepted within the community (Yu and Elderfield, 2007; Yu et al. 2007; Hendry et al. 2009; Yu et al. 2010; Rickaby et al. 2010; Allen et al. 2011).

Thirdly, because of small sample size Brown et al. (2011) could not explicitly analyze [Ca] matrix matched sub-samples as per Yu et al. (2005) and this study. Yu et al. (2005) demonstrated that the accurate determination of certain element ratios in foraminiferal is extremely sensitive to the [Ca] matrix of the samples relative to the calibration standards (e.g. Zn, Cd, U), whilst it is less important for other elements (e.g. Mg, Sr, Li). Our own work is consistent with the observations of Yu et al. (2005) and furthermore suggests that the accurate determination of foraminifera B/Ca ratios is highly sensitive to Ca-matrix effect (see right panel of Figure 1).

As we have explicitly determined O. umbonatus B/Ca using the [Ca] matrix-matched procedure (Yu et al. 2005), we are confident in the accuracy of our data relative to Yu et al. 2005, but acknowledge the lack of inter-calibration between labs may be another source of discrepancy with data presented in Brown et al. (2011).

We also note that Brown et al. (2011) adopted a number of steps that were different to the Yu et al. (2005) procedure adopted in this study, including the inclusion of a reductive cleaning step. The reductive cleaning step is a corrosive procedure that is known to lower some element ratios (e.g. Mg/Ca Barker et al. 2003, Yu et al. 2007) in foraminiferal calcite. The extent to which element ratios in foraminiferal tests are sensitive to reductive cleaning highly dependent on the metal ion and the species, reflecting species specific variations in test wall thickness and structure and also the heterogeneity of element ratios throughout test walls. To our knowledge there are no published studies that investigate the homogeneity of B/Ca in O. umbonatus, so it is not clear how this species will respond to the reductive cleaning step. Although Yu et al.

(2007) demonstrated that the reductive procedure did not appear to affect B/Ca ratios in three benthic species, this observation has not been established for O. umbonatus, therefore we have chosen not to include this corrosive reductive step.

Finally, in addition to analytical differences between our study and Brown et al. (2011), we question the basis of the evidence that lead Brown et al. (2011) to conclude that "Because of its infaunal habitat, B/Ca in O. umbonatus is largely insensitive to bottom water Δ[CO32-], and cannot be used for reconstruction of saturation states". We would argue that the amplitude of empirical regression coefficients alone is not sufficient to support their conclusion. The infaunal habitat of O. umbonatus will, to some extent, reflect the buffering of pore waters B/Ca and Δ[CO32-] relative to bottom waters. However, the mechanism(s) through which foraminiferal B/Ca respond to ambient Δ[CO32-] is largely unconstrained, therefore it is perhaps premature to discount the utility of B/Ca-Δ[CO32-] empirical regression relationships until 1) the mechanisms relating ambient Δ[CO32-] and O. umbonatus B/Ca have been investigated (as we attempt in our Biogeosciences Discussions paper), and 2) relationships between bottom water and pore water Δ[CO32-] and B/Ca and the parameters influencing these relationships have explored further.

Referee comment: X/Ca Records and synthesis The authors fail to examine the X/Ca records in light of other published X/Ca records across the Cenozoic. This is essential to provide context for their interpretations and might help in examining their offsets in X/Ca records. See records below: Lear & Rosenthal 2006: Benthic Li/Ca record from ODP 1218 (19-35 Ma) Benthic Li/Ca records from ODP 806 (0-12 Ma) Delaney & Boyle 1986: Planktonic Li/Ca record from DSDP 305 (0-65 Ma) Brown et al. 2011: Benthic B/Ca record from ODP 689 and ODP 1262 (32-46 Ma) Lear et al. 2003 Benthic Sr/Ca record (0-65 Ma) Peck et al, 2010: Benthic Sr/Ca, Li/Ca, and Mg/Ca from ODP 1263 (32.8-33.8 Ma)

Authors comment: In reply the authors would like to note that:

The Brown et al. manuscript was not available during the writing of this manuscript (see above discussion)

Reference was made to the Lear and Rosenthal (2006) paper – see section 4. Discussion, p. 3801 lines 10 to 20.

Reference was made to the Lear et al. (2003) paper – see section 4. Discussion, p. 3803 lines 6 to 11.

Reference to Delaney and Boyle was not made in this manuscript as there are two key differences with the current manuscript – firstly, Delaney and Boyle used a different method of attaining Li/Ca ratios and at present it is not clear how accuracy and precision of the two methods compare. Secondly, the subject of the Delaney and Boyle paper was planktonic foraminifera whereas we have examined benthic foraminifera. There is substantial evidence within the literature that planktonic and benthic foraminifer may calcify via different mechanisms and having differing sensitivities to environmental parameters, i.e. B/Ca ratios in benthic foraminifera correlate with bottom water carbonate saturation, however, a similar relationship in planktonic foraminifera is more equivocal and is currently a topic of debate within the community (Yu and Elderfield, 2007; Yu et al. 2007; Tripati et al. 2011).

Reference to Peck et al. (2010) was not made in this manuscript as we have concentrated on Pacific basin records given the likely occurrence of both basinal gradients and potentially cryptic species. In addition, regional diachrony of biostratigraphic markers means there may be some uncertainty in the age models of the two sites.

Referee comment: How do the uncertainties in the age model affect the interpretation? Potential uncertainties in the ODP site 1209.

Authors comment: We acknowledge that there may be some uncertainties in the Site 1209 age model resulting from the regional diachrony of some biostratigraphic markers that are used in the age model (Dawber and Tripati, 2011). Site 1209 is not unique in this limitation and to some extent our hypothesis testing of using multi-proxies records from a single site was designed to reflect this. The magnitude of Eocene Pacific basin bottom water Δ[CO32-] changes (Tripati et al. 2005; Lyle et al. 2005; Lear et al. 2006) are suggested to be considerable, such that they may potentially act as chemostratigraphic markers that will aid comparison of Pacific basin records.

Referee comment: Missing data before 41 Ma – Li and B – yet biggest shift in Eocene (CAE-3) – why focus on CAE-4?? The best test of CO3 vs X/Ca is a longer-term record across the CAEs to evaluate the correspondence with the magnitude of X/Ca and events themselves – CAE-3 biggest!

Authors comment: We acknowledge the referee's comment, and note the these periods of records without B/Ca and Li/Ca was not through design but reflect the timing of analyses with respect to the development of the capabilities of measuring both B and Li at Cambridge University. The data presented in this manuscript was gathered towards the end of the PhD of CFD, during which the method of obtaining multi-element data progressed to measuring B/Ca and Li/Ca.

Referee comment: Dissolution – Site 1209 is clearly situated close to the long-term lysocline as evidenced by the multiple clay rich horizons visible in core photos. Is there a dissolution effect on X/Ca – is this assessed in the calibration? Primary versus secondary carbonate ion controls.

Authors comment: The authors acknowledge this comment and agree that at present, secondary carbonate ion controls that would result of post-depositional dissolution and recrystallisation is a limitation of our and other published paleo-bottom water Δ[CO32-] reconstructions. In Dawber and Tripati (2011) we discuss the potential limitations of post-depositional processes on foraminiferal element ratios, but at present there is no consensus as to the degree to which element ratios may be modified by these processes or methods through which the extent of these processes may be assessed. Further work to investigate non-destructive ways in which post-depositional processes

have influenced foraminifera element ratios are needed. However, we note that Yu et al. 2007) showed from analysis of planktic foraminifera from a depth transect that B/Ca ratios may not be strongly sensitive to water column dissolution, while other studies have shown that Mg/Ca ratios are sensitive to dissolution.

Referee Minor comments: see authors comment immediately below each point Figures 1 and 2 could be condensed into a single figure to prevent repetition of information.

We have placed the Δ[CO32-] secondary y-axis onto the relevant plots of Figure 2 and removed Figure 1.

In figure 3 a pCO2 record is presented yet there is seemingly no reference to this in the main text.

The compiled pCO2 record in Figure 3 illustrates the long-term changes in the global carbon cycle during the Eocene and is present to aid readers with a context in which to set our new records. We have added a sentence to explicitly reference the record in the text.

Title – more informative about implications or conclusions of study

The records presented reflect reconstructions for one site and for a specific time period and therefore represent the first step of many that are needed for a full and thorough assessment of the element ratio proxies. It would perhaps be premature and misleading to make strong statements about the implications of the records or utility of the proxy in the title of the manuscript, given that the main conclusion of the paper is that caution is needed when applying these proxies and that additional work is needed.

Redundant' use of Mg/Ca: : :. To make correlations or lack of more readily digestible the authors would benefit from correlation coefficients between the different element ratios. Acknowledged, however the number of samples that have coeval ratios for all four element ratios is relatively small compared to the number of data points in the downcore records (a result of the evolving method of data acquisition as mentioned).

However, we now have a table showing what the R2 and p values are, and reporting n number of samples.

Typo fig caption 1 – O. umbonatus Corrected

Specify which ocean basin the CCD reconstruction is from in Fig. 2 Corrected

Typos Lyle et al., (2005) not 2006 Corrected

In abstract – mention that umbonatus is a benthic foram in the abstract Corrected

Edgar et al., 2007 references but not in list Corrected

Authors need to add a,b or c to their 2011 reference list. Corrected

Sentence starting on line 19 completely throw away move to methods. Clarification needed on which page the line 19 comment is referring to.

Line 23 – poor English please rephrase – "the site was above the CCD for much of the Eocene" Corrected

Foram preservation – authors state 'non-chalky' as opposed to what? I don't think the samples are glassy. Please be more specific. We have added a sentence on this and refer to further discussion in Dawber and Tripati (2011)

Consistency with number of decimal places that ages reported to e.g., line 9 on p3802. Corrected

Reply to Anonymous Referee 2 comments:

Referee Comment: LACK OF A SIMPLE DCO3= CONTROL ON X/CA

The major issue with this manuscript is that the trace element ratios studied are setup as recording DCO3=, despite the fact that a quick look at Figure 1 shows that there is clearly not a single control on these data. The authors clearly realise this, and spend the rest of the manuscript trying to find ways out of the assumed X/Ca to DCO3= relationship. However the manuscript would be far clearer, more useful and more citable

if this lack of a single control was clearly stated at the start of the results and the discussion, and if the phrasing of the results and discussion in terms of DCO3= changes was avoided. The potential influence of DCO3= should be discussed, but only in the same way that temperature, seawater chemistry etc. are. This general change will, I think, place the paper more safely back in the calibration category for these novel data, where they can make a useful contribution. For instance, several of these ratios have been applied in isolation as proxies for DCO3= or temperature, or have been used to make corrections on each other to try and isolate these competing factors. This dataset offers the opportunity to give a frank assessment of these approaches for this particular species.

Authors comment: The authors appreciate the referee's comments regarding the structuring of the manuscript and the manner in which data is presented. We acknowledge that some reorganizing is required to clarify our hypothesis and the steps taken to evaluate the data. However, the temperature and seawater composition of intermediate waters during the middle Eocene are still a matter of debate, and given these uncertainties, it is probably unwise to use these datasets and this time period as a basis for a comprehensive assessment of parameters influencing O. umbonatus element ratios in the context of proxy calibration.

We think that the approach we have taken, to set up a hypothesis of reconstructing middle Eocene Δ[CO32-] based on several different proxies, and then to evaluate the parameters that may cause the observed deviations specific to these records, is more conservative and fitting to the uncertainties associated with all the proxies. The purpose of this contribution is to illustrate that caution is needed when using O. umbonatus element ratio proxies to investigate the palaeoclimate of this period and to highlight that the proxy systematics require further investigation.

Referee comment: MULTIVARIATE ANALYSIS One of the most interesting approaches in this paper was the first application to foraminifera X/Ca of the global minimisation technique used by Gaetani et al. for coral X/Ca (Section 4.2), along with the multiple linear regression of core-top data (Section 4.1.1). However the data used in this regression analysis need to be shown and plotted, and the results of the global minimisation should also be shown - we are just given a description and table of parameters, without seeing the relationships involved.

Authors comment: Details of specific analyses are now illustrated.

Referee comment: CORE-TOP PAPER Furthermore, it seems that the more appropriate place for the multiple linear regression (which is based on core-top data) would be the author's current Biogeosciences Discussions manuscript, which discusses controls on X/Ca in core-top O. umbonatus Dawber and Tripati, 2012. Relationships between bottom water carbonate saturation and element/Ca ratios in coretop samples of the benthic foraminifera Oridorsalis umbonatus. . Tweaking which content is included in each manuscript would make both papers stronger: a decent discussion of the effect of temperature and pore water chemistry is needed in the core-top paper, and would be more appropriate there than here. Furthermore, this would allow both papers to be more a discussion of different potential effects, rather than pitching the core-top solely in terms of DCO3=, which is taken up at the start of this manuscript, and then has to be taken apart.

Authors comment: The core top manuscript by design does not span a wide range of bottom water temperature or seawater composition, and only investigated the influence of saturation state on the proxy. The motivation for structuring the core-top paper was in the context of studying biomineralisation mechanisms.

However, as suggested, we now also add the multiple linear regression based on core-top data to the BGD manuscript for comparison, and also include it in this paper.

Referee 2 Specific comments:see author comment immediately below

Most of my specific comments relate to repeated phrasing of the different changes observed in the different X/Ca in terms of DCO3=, and to my difficulty in see the cor-

relations in the data that the authors describe in the text. [3796, 16: suggests that DCO3= IS the dominant control for all of Li/Ca, B/Ca and Sr/Ca. 3800, 18: found some of these changes very hard to see. 3800, 23: is there really more variability, or just more data? 3802, 11: the Sr/Ca changes seem small compared to the scatter 3802, 22: again, I'm afraid I don't see this relationship: the Sr is pretty flat, and the only variations within the CCD record seem to show anti-correlations with Li and Sr, if anything at all. 3804, 23: they all seem different to each other - Mg/Ca doesn't seem to stand out. 3806: very hard to see these correlations. 3802, 4: again, discrepancies between ALL the X/Ca data!

The re-structuring of material in the manuscript, the amended figures and additional statistics in tables should clarify these issues.

3697, 6: and shorter than weathering/volcanic degassing timescales (106; 107) Noted, additional text has been added to clarify this point.

3797, 14: though linking intermediate water DCO3= to pCO2 may always be difficult. Biggest differences in mid-depth DCO3= in the modern ocean are a function of ventilation and productivity (compare North Atlantic to North Pacific at 2000 m). Still, guess it's worth a shot... Acknowledged, and we have added a sentence to include reference to these additional parameters.

3798, 5: how many tests? The range of number of foraminifera tests used in the analyses has been added.

3798, 7: don't think the reference to the "standard Cambridge oxidative procedure" adds much to those not at Cambridge - best to stick to the reference to Barker. Corrected

3798,9: what concentration were solutions measured at? Reference to 100 ppm Ca concentration solutions has been added

3798,16: give these values The list of values is documented in Barker et al., (2003).

3799, 10: out of interest, do you see any difference between well preserved and poorly preserved samples? As discussed in Dawber and Tripati (2011) the preservation of foraminiferal tests can vary within a sample. We have taken care to select the best-preserved specimens. A specific study examining a larger number of coeval samples is required to address this comment.

3800, 3: don't think this section should be phrased in terms of DCO3=, as discussed above. We acknowledge this comment and refer to our reply above about the structuring of the manuscript above.

3800, 13: some discussion of the short term variability would be good - is there any correlation here between the X/Ca ratios or any other parameters? Perhaps try subtracting the long term trends and making cross plots of the different ratios - could be a good examination of any common controls. Would be good to show a zoomed in plot. We had previously explored cross plots of the different element ratios, however differences in the residence time of the cations in seawater and potentially the timing of changes in seawater cation concentration make comparisons of this type difficult without alternative proxy constraints on the timing of such changes.

3801, 5: could do with another subheading here (something like Comparison to other carbonate system records) and again, less discussion in terms of DCO3=. 3801, 8: but again, almost all of the implied changes in DCO3= are different! Acknowledged. See comments above regarding structuring of the manuscript

3801, 14: this study may suffer from the same issue as seen here and in the author's BGD manuscript: the changes seen in the specific locations where DCO3= changes are big over a small range of temperature may not apply to more general locations, where big changes in DCO3= and temperature may occur. We acknowledge this comment but also note that it is necessary to set the context of our core top regressions with regards to published literature.

3802, 17: the phrasing of this seems to be the wrong way round: d13C and wt percent

organic carbon would be most likely to be PRIMARILY controlled by CaCO3:Corg rain rate, which may have some control on DCO3=.

3803, 9 - 16: this is a massive stretch and really doesn't add anything - should be cut. We acknowledge this comment, however as this is the first study to use these four element ratio proxies, we feel it is important to make use of all available data in order for comparison.

3804, 5: again, should be in core top, and actually shown. This data is currently also included in the core top manuscript and as we acknowledged in the comments above, some re-organisation of the material included both the core top and down core manuscript is necessary.

3804, 12: what diagenetic alteration in core tops? Here we refer to the comments of Marchitto et al., (2007) that some of the benthic foraminiferal Mg/Ca data presented in Lear et al., (2002) from the Little Bahama Bank, may be biased due to the presence of secondary calcite.

3805, 4: what does vacuolisation have to do with this? Surely the point is that seawater is the starting solution. Yes, and this is the idea that we stress in this sentence.

3806, 19: different diagenesis and dissolution histories could also affect these X/Ca differences. This is a good point that we have incorporated.

3807, 5: again, this section needs a figure, which should also indicate which data are excluded. Now included, see comments above.

3807, 20: *this nicely makes the point that there is not a common control (or even couple of controls) or these data* Acknowledged.

3808: this section is needed in the core-top paper, especially once the core-top O. umbonatus B/Ca data of Brown et al. 2011, EPSL and Rae et al. 2011, EPSL are considered. This will include some discussion on pore water chemistry in the core top manuscript but also feel this discussion is necessary in the downcore manuscript also.

3808, 4: and measurements, e.g. Archer et al., 1989, GCA. This reference is now included.

3808, 21: no, borate speciation and DCO3= will go together - they have the same controls, unless there are very significant changes in porewater B/Ca. Changes in X/Ca in pore water is a potential issue that could be discussed. These issues are acknowledged and more discussion has been added.

3808, 24: and other infaunal species in Rae et al. 2011, EPSL. This reference is now included.

3809, 3-5: no, we really can not make this claim from these data. On review, this sentence has now been removed.

3809, 20: as above, local changes in productivity and ventilation are likely to have the largest effect on DCO3= at these depths. We have added a sentence to discuss this possibility.

3810, 12: don't think anyone has successfully cultured deep sea forams like O. umbonatus. This is also our understanding, but in order to further assess the parameters influencing foraminiferal elemental ratios it is necessary to try approaches other than the empirical core top regression analysis. Culturing presents an alternative method, but will be challenging and new techniques may be required to culture deep-sea species.

FIGURES Figure 1: - Would be helpful to see the d18O stack for reference. - Don't think it's appropriate or helpful to show the DCO3= scales - too much interpretation for this first figure. - Show representative error bars. Figure 2: Labels are too small. weight percent CaCO3 and fragmentation are compared several times - would be better to have them adjacent, then CCD, then Corg. These comments have been reviewed in the figures.

Technical corrections 3797, 23 and elsewhere: does this need to be Dawber and Tripati, submitted? Corrected

3800,1: sort syntax here.?

3800, 16: could cut the "measurements ... prior to 41 Ma" bit We feel this sentence is necessary, as other reviewers have questioned why B/Ca and Li/Ca records are less extensive than the Mg/Ca and Sr/Ca records.

3804, 18: A similar approach Typo corrected

REFERENCES: A paper by Edgar et al. 2008, which is cited in the text, is not included here. Check for other omissions too. Corrected

Interactive comment on Clim. Past Discuss., 7, 3795, 2011.

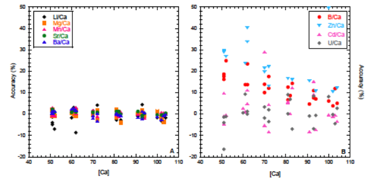

Figure 1. Metal/Ca ratios expressed as accuracy percentage ((measure ratio-actual ratio)/ actual ratio)*100). Element/Ca ratios that do not exhibit a Ca induced matrix effect are shown in panel A and include Li/Ca, Mg/Ca, Mn/Ca, Sr/Ca and Ba/Ca, and those that do display a matrix effect are shown in panel B and include B/Ca, Zn/Ca, Cd/Ca and U/Ca. Analyses are based on diluted standards which have B/Ca ratios of 31 and 60 μmol/mol respectively (which brackets the range of B/Ca ratios observed in *O. umbonatus*), Li/Ca = 2.0 and 4.0 μmol/mol, Mg/Ca = 0.217 and 0.603 mmol/mol, Mn/Ca = 11.7 and 21.3 μmol/mol, Zn/Ca = 1.37 and 2.32 μmol/mol, Sr/Ca = 0.506 and 0.803 mmol/mol, Cd/Ca = 0.024 and 0.055 μmol/mol, Ba/Ca = 1.6 and 2.11 μmol/mol and U/Ca = 1.1 and 3.1 nmol/mol.

Fig. 1.