

## ***Interactive comment on “Calcium isotopic composition of high-latitude proxy carrier *Neogloboquadrina pachyderma* (sin.)” by D. Hippler et al.***

### **Anonymous Referee #2**

Received and published: 12 November 2007

Review of Hippler et al

This is an interesting paper that attempts to expand the use of Ca isotopes as a temperature proxy into high latitudes by investigating Ca isotope fractionation by *N. pachyderma* (sin). Although the paper is only just a calibration between temperature and Ca isotope fractionation in one species of foraminiferan, there are two notable things about it. First, it separates the water column samples at least into different genetic strains and looks for variability between them in Ca isotope fractionation. Second, it demonstrates, in a single study of a single species of foraminiferan, what has been seen in different studies and has been impossible to reconcile- that sometimes a strong dependence

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of Ca isotope fractionation on temperature is seen and sometimes no relationship is found at all.

The sour note to the manuscript is that it is written from the unabashed point of view that the "right answer" is that there is a strong dependence of temperature on Ca isotope fractionation. What the paper is most crucially missing is a thorough consideration of why temperature dependence of Ca isotope fractionation ceases to occur at lower temperatures. And the paper should consider whether its observations have any bearing on the conflicting results about the temperature dependence of Ca isotope fractionation in temperate species.

### Big comments

1) M&M section- Not enough information is given about the chemical preparation of samples for mass spectrometry nor about the mass spectrometry itself. No one has yet eliminated analytical techniques as a cause for the contradictory observations of the influence of temp on Ca isotope fractionation. Given this and because few labs measure Ca isotopes, it would be best to report in sufficient detail the techniques utilized in Ca isotope studies. For this manuscript, this means giving information on the double spike (which isotopes, etc), the details of the mass spectrometry (e.g., number of blocks of how many integrations of how many seconds collected for each single measurement? how many replicate runs done for each data point?, etc), and on the samples preparation (what is the "chemical separation" alluded to in the text but not described?).

At least some bare minimum of detail should be given in addition to citing the older papers detailing the techniques in full.

2) There is something strange going on with the regressions calculated from the data. Using the same data, I get different lines. Probably the difference is that they have used a smaller subset of the data than I did, but it's impossible to tell this from their description of what they have done. It's also impossible to tell if the lines are meant to

be regressions or not, because they are never called anything more specific than "relationships" and correlation coefficients, sample sizes, nor levels of significance have been given. This is a serious issue, especially in a paper whose raison d'être is defining the "relationship" between Ca isotope composition and temperature for use as a paleoceanographic proxy!

For example, the "relationship" between  $\delta\text{Ca}$  and temperature for the northern North Atlantic specimens (Type I) is given as

**$\delta\text{Ca} = 0.23(\text{SST}) - 0.46$** . No correlation coefficient nor the sample size has been given.

Using a spreadsheet and the North Atlantic Ocean data in Table 1, I calculate a slightly different line:

**$\delta\text{Ca} = 0.16(\text{SST}) - 0.11$**  ( $r^2 = 0.54$ ,  $n = 15$ , correlation is significant at  $\alpha = 0.05$  but not 0.01 level)...

See Plot 1.

Likewise, I can't reproduce the line of

**$\delta\text{Ca} = 0.12(\text{SST}) - 0$**

reported for the S Atl (typ III) data. The curve I get is

**$\delta\text{Ca} = 0.09(\text{SST}) + 0.25$**  ( $r^2 = 0.66$ ,  $n = 11$ , correlation is significant at  $\alpha = 0.05$  but not 0.01 level)...

See Plot 2.

And so on.

And so I put in a firm plea for the authors to explain their calculations clearly. Specifically, they need to explain the calculation done in the ISOPLOT program, they need to clearly identify which data have gone into each curve, and they need to report the statistics (correlation coefficients, samples sizes, and whether or not the slope of the

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line is significantly different than 0).

3) It would be good to have error bars on the isotope-temperature plots, both for the isotopes and the temp estimates.

4a) The authors should consider the sediment core top data more explicitly than they do. It's exciting that much of it falls on the same temperature line as the live foram data do (see slope (on Plot 3) of non polar Nordic Sea core tops below versus Hippler et als' temp- $\delta$ Ca equation).

But it's also interesting that the entire set of core tops that the authors designate as polar on Table 2 fails to show any relationship to temperature at all. The authors brush this aside by saying that below 2°C, the relationship between temperature and Ca isotope fractionation no longer works. But this "critical temperature" is an observation but not an explanation. And it's not even clear from the results that it is the only plausible explanation. For example, another way to interpret the data in the above plot is that the two highest Ca isotope values are flyers and the line with the extremely shallow slope soundly describes all of the reported Nordic Sea core top data. It makes more sense after all to throw out two anomalously high numbers than it does to toss out 9 data points with fairly average values. It is fine for the authors to make the "ignore everything below 2°C" argument, but they must also consider the "two high flyers" alternative. Essentially, they are justifying the steep slope from the live foram data, but it is worth pondering the question if the sediment core tops are really showing that same relationship, or whether the temperature-Ca isotope relationship is being muted in between the water column and seafloor. (in considering this it would help to make it unambiguously clear on Fig 3 which are the core top and which are the live foram data!!! Right now, it's really hard to tell that on the plot).

4b) It is useful for the author's purposes of establishing a working calibration between Ca isotopes and T, to just say that it's fine to use the proxy above 2°C. But could the authors also provide some argument as to the mechanism that would result in a lack

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of expression of the temp dependence at 2°C? Some half-hearted mention is made of Mg/Ca studies at low temperatures, but the mechanism responsible for the flattening out of the Mg/Ca-temperature curve is not adequately discussed here. Nor have the authors discussed why the mechanism responsible for flattening out the Mg/Ca temperature response would affect Ca isotope fractionation too.

4c) Another thing that would be instructive would be for the authors to set their results for *N pachyderma* from core tops (or both water column and core top results) more fully into the context of the work that has been done on other species.

For example, it is quite interesting that their core top data don't look so very different from Sime et al., 2005's core top data for a bunch of different species (see below). The surprising correspondence of the values may mean nothing, or it may suggest that the interpretation of the 2°C limit of expression of the temperature dependence is a fallacy. This needs to be explored in the paper!

See Plot 4.

### Small comments

A general small comment: For the most part, the paper is well written, but it often slips into a bit of grammatic confusion. The most distracting of the errors are pointed out below, but the manuscript needs more proofreading than this.

1) Intro: Celsius is misspelled.

2) Section 2.1 and 2.4: "genetically determination" should be "genetic determination".

3) M&M section- Sometimes the text slips inappropriately into the present tense (e.g., "Samples chosen for genetically (sic) determinations *belong* approximately to the 125-250 um size fraction" would be better as "Samples chosen for genetic determinations *were taken* from the 125-250 um size fraction").

The same is true in the results section.

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4) There is a general dearth of commas in the paper.

For example, they are often missing after introductory phrases. Some examples of sentences in this category:

Concerning the core top samples, approximately...

In this approach, potential inter-individual...

Other places where commas are missing include:

The geochemical signatures of carbonate skeletal remains, i.e. foraminifera {the correct plural form of foraminifer is foraminifers or foraminiferans, btw. Foraminifera is the name of the taxonomic phylum.}, corals, and bivalves, provide...

The accurate reconstruction of the SST history is therefore essential for climate modelling (Rahmstorf, 2002), yet.....

And so forth...

5) Results- Is there any reason to leave the Sime et al 2007 paper off of the list of papers (Fantle and DePaolo, 2005 and Heuser et al., 2005) showing negligible change in the Ca isotope composition of seawater during the Pleiocene and Pleistocene?

6) Results- The phrase, "... a potential inherited genotype dependency on Ca isotope fractionation..." literally means that the genotype is dependent upon Ca isotope fractionation. What the authors are actually trying to say that the magnitude of Ca isotope fractionation might be dependent on genetic factors. This needs to be fixed. And, actually, the whole sentence is ungrammatical (as the way it is written implies that four foraminiferans are testing the potential for variations in Ca isotope fractionation being linked to genotypes... rather than it being the researchers who are using four different genotypes of foraminiferans to test whether or not the magnitude of Ca isotope fractionation varies between genotypes of the same morphotype).

7) By convention, shouldn't latitude precede longitude in Tables 1 and 2? It's confusing

to have Long first.

8) There is some confusion on Fig 3 as to which symbols are core tops and which are genotyped samples (the caption and legend disagree). Also is the fact that the symbols come in different sizes meant to convey information? It's a bit distracting, so if the size difference doesn't convey information, it should be gotten rid of.

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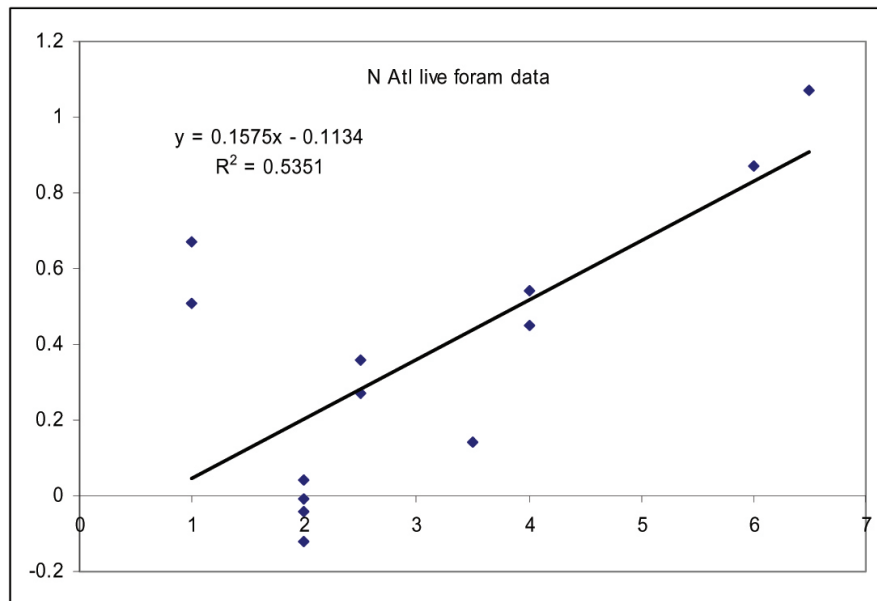
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Figure 1:

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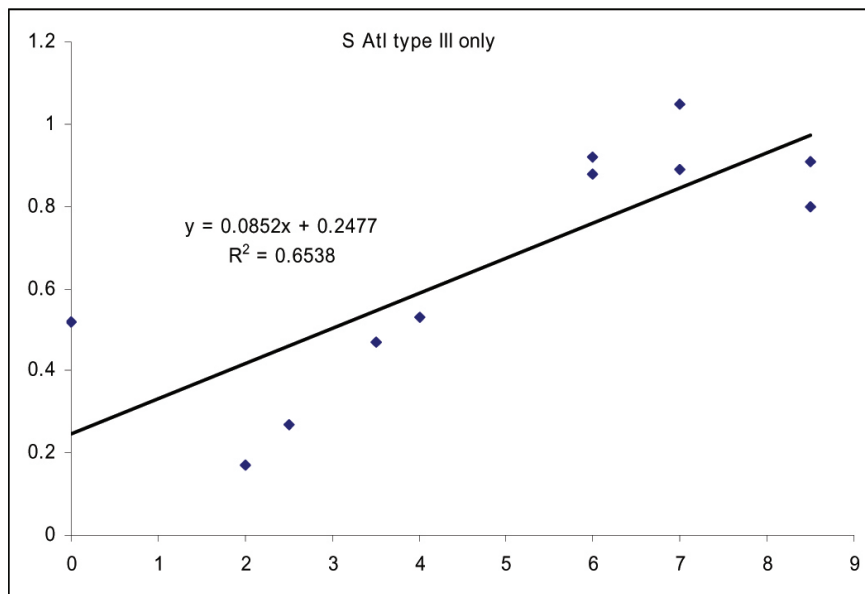
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Figure 2:

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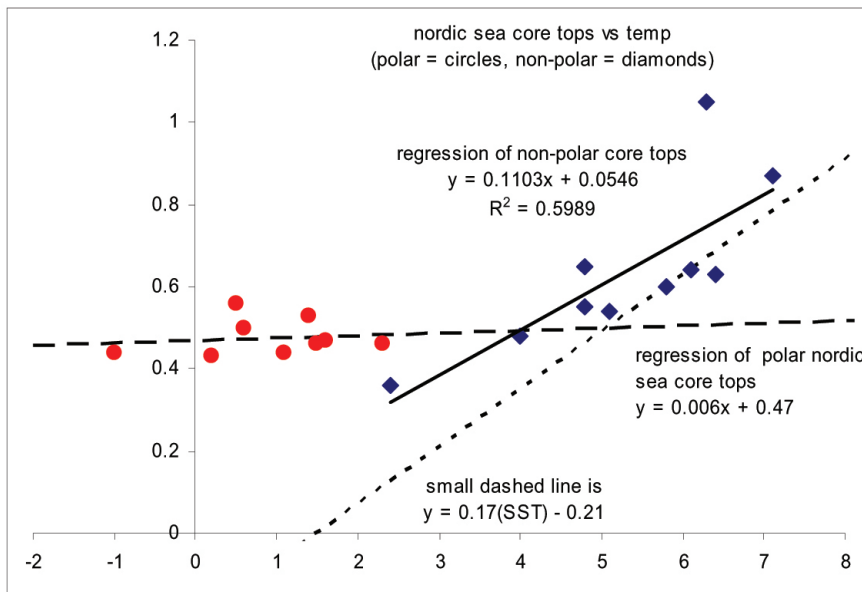
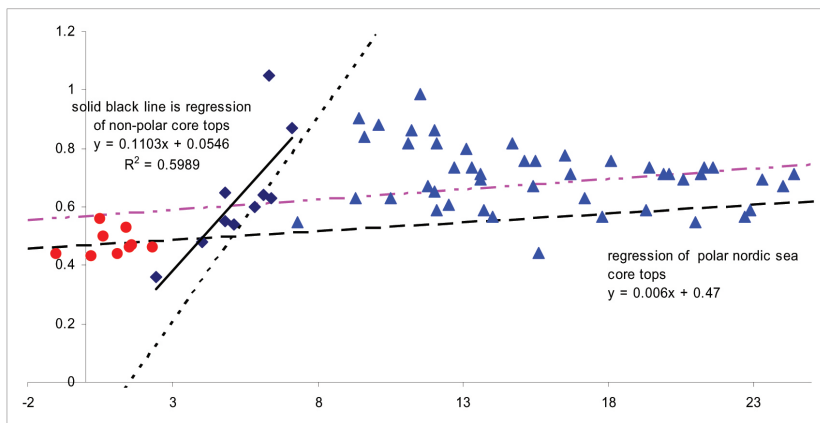


Figure 3:



polar = circles, non-polar = diamonds, Sime et al = triangles  
 solid line = nonpolar N pac core top regression  
 dotted line = hippler et al global N pac temp Ca isotope line  
 dashed line = non polar n pac core top  
 dashed and dotted line = all core tops except non polar n pac ( $y = 0.007SST + 0.57$ ,  $r^2 = 0.18$ ,  $n = 62$ , slope not significantly different than 0 at alpha equals 0.5 or 0.1)

Figure 4:

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