Biogeosciences Discuss., 4, S1643–S1649, 2007
www.biogeosciences-discuss.net/4/S1643/2007/

Biogeosciences Discussions

Interactive comment on "Early diagenetic overprint in Caribbean sediment cores and its effect on the geochemical composition of planktonic foraminifera" *by* M. Regenberg et al.

M. Regenberg et al.

Received and published: 17 October 2007

Author comments to Referees D. Lea and J. Bijma. General comments regarding Biogeosciences Discussions, 4, 2179–2213, 2007: "Early diagenetic overprint in Caribbean sediment cores and its effect on the geochemical composition of planktonic foraminifera" by M. Regenberg, D. Nürnberg, J. Schönfeld and G.-J. Reichart. Reviewer comments are given prior to our answers; the revised text is reported between quotation.

D. Lea: It would be useful to add some discussion about why some Caribbean sites display this phenomenon and others do not. Or is it possible that in other sites there is a very slight level of recrystallization that could significantly affect the climatological interpretations?

J. Bijma: On p. 2191 you state: "..show to some extent atypical values with respect to previously published data sets reflecting past environmental conditions (Figs. 4, 5)." It is clear that your data are atypical with respect to the published ones. Yet, it might be usefull (although not necessary) to state why the published records reflect the "true" environmental conditions.

R.: It is common sense that diagenetic alteration from carbonate overgrowth biases δ^{18}O "to more positive values (e.g., Killingley, 1983; Schrag et al., 1995; Crowley and Zachos, 2000; Pearson et al., 2001; Wade and Kroon, 2002)" [Chapter 4 in the revised manuscript]. Such effect on δ^{18}O was actually observed for deep-sea sediments, "yet merely for sample material from greater sediment-burial depth (e.g., Pearson et al., 1997; Norris and Wilson, 1998; Price et al., 1998; Wade and Kroon, 2002; Tripati et al., 2003; Sexton et al., 2006)" [Chapter 4 in the revised manuscript]. It certainly is possible that sediments even from the topmost meters of other regions are affected by precipitation, like shown for sites M35027 and M35053 in Figure 5. Yet from the "occurrence of anomalously high Mg/Ca above 6 mmol/mol, only when HMC is absent from the sediments" [Chapter 4.2 in the revised manuscript], we conclude that the vicinity of carbonate platforms is crucial to diagenetic alteration of the kind we found in our cores.

D. Lea: In this respect, it would be very valuable if the authors could list criteria researchers could use to evaluate if forams from a particular core have experienced recrystallization, both major as observed here or perhaps more subtly. This would be particularly valuable in the form of a preliminary test that could be made prior to major investment in research on a particular core. With respect to this issue, it would appear that the Sr/Ca data is the most unambiguous indicator of recrystallization. The authors might add some further discussion what controls Sr in forams (Lea et al., 1999, GCA, Russell et al 2004, GCA) and about how the observed altered Sr/Ca values compare to published downcore records of Sr/Ca in the literature. Sources might include Martin et al 1999 G3 and Elderfield et al 2000 G3. The quantification of how an observed

BGD
4, S1643–S1649, 2007

EGU

Sr/Ca depletion is related to %recrystallization could be quite valuable, for example, in assessing how much a particular δ^{18}O record has been shifted by recrystallization. In this context it might be useful to discuss the range of published Sr/Ca values for each species and how definitively a particular degree of recrystallization can be picked up by an observed Sr/Ca depletion (see the above cited refs and others for what factors control Sr/Ca in downcore records). It would be valuable to present a minimum Sr/Ca value for a particular species in this setting below which one could confidently state that some degree of recrystallization had taken place.

R.: We agree that Sr/Ca may serve as sensitive indicator of calcite overgrowth due to small intraspecific ranges for planktonic foraminifera. From uncertainty about Sr/Ca variation between foraminiferal species, nevertheless, it is only possible to set the lower tolerance for Sr/Ca to 1.2 mmol/mol. "Depending on the species, typical Sr/Ca of recent core-top planktonic foraminifera without overgrowth are in the order of 1.2–1.7 mmol/mol (Figure 6), which is in good agreement with literature specifications (e.g., Lea et al., 1999; Russell et al., 2004; Elderfield et al., 2000; Kunioka et al., 2006). In general, foraminiferal calcite is supposed to record Sr/Ca of seawater (Delaney et al., 1985), which changes on glacial/interglacial time scales (e.g., Graham et al., 1982; Stoll and Schrag, 1998). Sr/Ca is relatively homogeneously distributed throughout the test (e.g., Brown and Elderfield, 1996; Anand and Elderfield, 2005) and is affected by other factors like temperature, pH, and salinity with an absolute Sr/Ca variation of 15% (e.g., Lea et al., 1999; Russell et al., 2004; Anand and Elderfield, 2005; Kunioka et al., 2006). However, since biogenic calcite contains significantly more Sr^{2+} than inorganic (Baker et al., 1982; Carpenter and Lohmann, 1992), the low Sr/Ca observed in this study indicates significant proportions of secondary inorganic calcite attached to the foraminiferal test (Bralower et al., 1997)." [Chapter 4.1 in the revised manuscript] "In accordance with downcore Sr/Ca records (e.g., Martin et al., 1999; Elderfield et al., 2000), we propose the lower level for Sr/Ca to exclude alteration by diagenetic calcite for at least Mid-Pleistocene to Holocene of planktonic foraminifera to be as high as 1.2 mmol/mol. However, caution has to be exercised on apparent interspecific variation,

BGD
4, S1643–S1649, 2007

EGU

which may elevate this lower level." [Chapter 5 in the revised manuscript]

D. Lea: Other points: 2180-2181: I would say that over printing of the forams by coatings is another important diagenetic process that affects foram composition. See discussion going back to Boyle (1983) through Pena et al (2005) G3.

R.: Although coatings are not involved in diagenetic processes of this particular issue, they play an important role in the alteration of the primary Mg/Ca. "Secondly, the geochemical composition may be altered by reprecipitation of calcite from sediment pore fluid (e.g., Baker et al., 1982; Norris and Wilson, 1998; Hover et al., 2001; Rudnicki et al., 2001) and manganese/iron (hydr)oxide coatings (e.g., Boyle, 1983; Reichart et al., 2003; Pena et al., 2005)." [Chapter 1 in the revised manuscript]

D. Lea: The discussion of how the recrystallization takes places seems somewhat vague and unspecific.

R.: We agree that the process of diagenesis itself is relatively indefinite. Due to the lack of pore-water data for the presented sites and generally little knowledge of shallow-burial diagenesis of deep-sea sediments from the literature, the process of recrystallisation remains unclear. "The early diagenesis of pelagic carbonates has initially been thought to be entirely mechanical compaction down to the ooze-chalk transition zone at approximately 140–200 m sediment depth (e.g., Neugebauer, 1973). Dissolution and reprecipitation of calcite as euhedral calcite crystals inside foraminiferal chambers was observed in samples from below that level (e.g., van der Lingen and Packham, 1975). Model calculations considering pore fluid chemistry, and observations from Antarctic shallow water deposits revealed that early diagenesis may commence at much shallower depth in the sediment (Schrag et al., 1995), and that planktonic foraminifers are far more sensitive than other sedimentary components to chemical alteration (Barrera et al., 1987). Recent evidence from sediment cores from the Greenland Sea revealed that this process may occur even at 460 cm below the seabed, and that the calcite overgrowth substantially biased the original environmental signal recorded in foraminiferal

BGD
4, S1643–S1649, 2007

EGU

tests (Millo et al., 2005). Their results credence credibility to our observations." [Chapter 4.1 in the revised manuscript]

J. Bijma: The crystalline overgrowth is estimated to amount to 10 to 20% by weight. This observation has important implications as well for the study using so called "size normalized weight" (SNW). In fact, SNW may help to estimating the potential geochemical contamination at your site.

R.: Analysis of test weights was performed for low-resolution site SO164–19–2. Unfortunately, the relation between Mg/Ca and test weight is not straightforward, we are forced to apply mass balance in order to estimate the amount of diagenetic calcite. "The average test weight of *G. sacculifer* from site SO164–19–2 generally shows an increasing trend with time. From ∼33–40 μg in the youngest part, weights increase to ∼36–45 μg in the interval between MIS 6–10 and to ∼38–50 μg prior to MIS 12 (Figure 4). Very high (low) Mg/Ca (Sr/Ca) at transitions MIS 10/11 and MIS 12/13 are coinciding with highest test weights of ∼50 μg and ∼55 μg, respectively. Yet, MIS 11 and 12, characterized by highest (very low) Mg/Ca (Sr/Ca), are accompanied by very low test weights of only ∼34–41 μg." [Chapter 3.2 in the revised manuscript]

"Tests of the same species and size are assumed to have relatively constant initial weights before sinking to the seafloor (e.g., Barker and Elderfield, 2002). Decreasing test weight is positively correlated with the seawater carbonate ion concentration (e.g., Lohmann, 1995; Broecker and Clark, 2001) and accompanied by changing geochemical composition of the test (e.g., Rosenthal and Lohmann, 2002; de Villiers, 2003). Unfortunately, covariation of increased foraminiferal test weights and Mg/Ca or Sr/Ca, respectively, is not straightforward in this study, for instance during MIS 11 and 12 (Figure 4). Thus, it is improbable to assess reasonable amounts of attached diagenetic calcite by size-normalized test weights. Our approach to estimate the proportion of diagenetic overgrowth necessary to alter the foraminiferal Mg/Ca and Sr/Ca (Figure 4) is to apply a mass balance." [Chapter 4.1 in the revised manuscript]

BGD

4, S1643–S1649, 2007

J. Bijma: On page 2183: "....foraminifera *Globigerinoides sacculifer* (without sac-like final chamber)". I know that this is used by everybody in this way and therefore leave as it is but *G. sacculifer* without a sac-like final chamber is stricktly speaking *Globigerinoides trilobus*.

R.: "Planktonic foraminiferal specimens resembling *G. sacculifer* (Brady, 1877) in shape and morphology but without a sac-like final chamber were nominated as *Globigerinoides trilobus* (Reuss, 1850) in many papers since the 1960s (e.g., Bé and Hamlin, 1967; Hecht, 1974; Lončaríc et al., 2006). On the other hand, both species were lumped in paleoceanographic studies and *G. trilobus* was assigned to *G. sacculifer* as a morphological variety without sac-like chamber (e.g., Koutavas et al., 2002; Sime et al., 2005). Indeed, culture experiments revealed that the formation of a terminal sac-like chamber in *G. sacculifer* preceeded gametogenesis, but gametogenesis did also take place without the development of a sac-like chamber. Darkness and the presence of vital symbionts in the cultured specimens had also significant effects on the frequency of sac-like chamber formation (Bé et al., 1982). Considering these experimental data, it is rather unlikely that the *G. trilobus* morphotype represents an biological entity different from the *G. sacculifer* morphotype. *G. sacculifer* and their ability to form sac-like chambers evolved after the origin of *G. trilobus* in the early Miocene (Keller, 1981). As such it is justified to determine Pliocene to Holocene specimens with or without a sac-like chamber as *G. sacculifer* (M. Kucera, Tübingen, pers. comm.)." [Chapter 2 in the revised manuscript]

J. Bijma: corresponding to temperatures of 32.2°C and 33.1°C, respectively." Please add that planktonic foraminifera, or at least the species you analysed, are not very likely to survive those temperatures (Bijma et al., 1990).

R.: "From this level, Mg/Ca increases to as much as 6.66 mmol/mol during MIS 5e and 7.13 mmol/mol during MIS 7, corresponding to temperatures of ∼32.2°C and ∼33.1°C, respectively, which approaches the upper temperature tolerance of these species (Bijma et al., 1990)." [Chapter 3.3 in the revised manuscript]

BGD

4, S1643–S1649, 2007

Interactive Comment

J. Bijma: The figures 7 and 8 do not clearly support the text.

R.: The assignment of scanning-electron microscope pictures was subject to misunderstanding. Thus, we rephrased mainly the figure captions in the revised manuscript. "Figure 7. SEM images of the wall-surface texture of opened planktonic foraminiferal chambers: a) *G. ruber* w. of site SO164–07–4, 118 cm (∼23 kyrs) with typical Mg/Ca, uncleaned; b) *G. ruber* w. of site SO164–19–2, 130 cm (∼259.5 kyrs) with anomalous Mg/Ca, cleaned; c) *G. sacculifer* of site SO164–07–4, 118 cm (∼23 kyrs) with typical Mg/Ca, cleaned; d) *G. ruber* w. of site SO164–19–2, 260 cm (∼473 kyrs) with anomalous Mg/Ca, cleaned; e and f) *N. dutertrei* of site SO164–19–2, 315 cm (∼563.5 kyrs) with anomalous Mg/Ca, uncleaned and cleaned, respectively. Mg-cleaned samples, whether with or without overgrowth, show smoothed edges due to the intense cleaning protocol. Scale bar = 10 μm."

"Figure 8. SEM images of wall-cross sections of opened planktonic foraminiferal chambers: a) *N. dutertrei* of site SO164–07–4, 3 cm (∼0.9 kyrs) with typical Mg/Ca, uncleaned; b) *G. ruber* w. of site SO164–19–2, 260 cm (∼473 kyrs) with anomalous Mg/Ca, uncleaned; c) *G. ruber* w. of site SO164–07–4, 3 cm (∼0.9 kyrs) with typical Mg/Ca, uncleaned; d) *G. ruber* w. of site SO164–19–2, 260 cm (∼473 kyrs) with anomalous Mg/Ca, cleaned. Scale bar = 10 μm."

Interactive comment on Biogeosciences Discuss., 4, 2179, 2007.