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Discussions

Interactive comment on "Reconstruction of secular variation in seawater sulfate concentrations" *by* T. J. Algeo et al.

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Received and published: 24 January 2015

NOTE: SEE SUPPLEMENTARY DOCUMENT FOR FULLY FORMATTED REVIEW-AND-RESPONSE

Comments by U.G. Wortmann

General Comments

I have read the paper by Algeo et al with great interest. The authors discuss ways to derive the concentration of sulfate in seawater from the stable isotope ratios observed in sulfides and sulfates. Attempts to do this date back decades, and it is commonly believed that the seawater sulfate concentration varied considerably through time. However, data (as opposed to interpretations) is restricted to a few Cenozoic samples.

Some fluid inclusion data exists for the Mesozoic, but it is no longer primary data as their interpretation relies on un-testable assumptions about the chemical composition of Mesozoic seawater.

Response: We thank Dr. Wortmann for a constructive review, in which a number of important issues were raised.

The authors present two different approaches to estimate the marine sulfate concentration. The first one is based on the rate of change of the observed S-isotope ratio, and basically states that if we assume that modern burial/weathering fluxes are representative, the rate of change is a measure of the reservoir size (aka sulfate concentration). As far as I understand it, this approach is only valid if the rate of change is equal to the residence time of the respective system. The authors allude to this somewhat obliquely on page 13192, line 8ff. However, what happens if the fluxes become so big that the rate of change is considerably faster then the residence time, and even affect the reservoir size itself?

Response: First, the mathematical relationships underlying the rate method deserve clarification. The reviewer's comment above, taken literally, is incorrect. Rate of change has units of per mille per million years (‰ Myr^{-1}) and therefore cannot be "equal to" residence time, which has units of Myr^{-1}. We infer the reviewer's intended meaning to be that the maximum possible rate of change in seawater sulfate $\delta 34S$ (i.e., $\partial\delta 34S_{SO4}/\partial t (max)$) is inversely proportional to residence time (t):

$\partial\delta 34S_{SO4}/\partial t (max) \equiv t\hat{\,}{-1}$ [or $t \equiv \partial\delta 34S_{SO4}/\partial t (max)\hat{\,}{-1}$] (B0)

The exact quantitative form of this relationship can be derived from Equation 2 of Algeo et al. (2014), reorganization of which yields:

MSW / FPY = k1 × D34SCAS-PY / $\partial\delta 34SCAS/\partial t (max)$ (B1)

[Note that here and in subsequent equations, MSW is 1.3 × 10ˆ21 g, FPY has units of g yrˆ-1, D34SCAS-PY has units of per mille (‰, $\partial\delta 34SCAS/\partial t (max)$ has units of ‰

Myr^{-1}, t has units of yr, and k1 and k2 are constants equal to 10^6 (no units) and 2.22 × 10^{-20} mM g^{-1}, respectively (see Algeo et al., 2014, for further explanation).] The residence time of sulfur in seawater is equal to the mass of seawater sulfate divided by the total sink flux, i.e., the reduced sulfur flux (FPY) plus the oxidized sulfur flux (FEVAP):

t = MSW / (FPY + FEVAP) (B2)

Letting XPY be the fraction of the total S flux represented by pyrite burial (i.e., FPY / (FPY + FEVAP)), then:

t × XPY^{-1} = MSW / FPY (B3)

And substitution into Equation B1 yields:

t × XPY^{-1} = k1 × D34SCAS-PY / ∂δ34SCAS/∂t(max) (B4)

Equation A5 thus quantifies the inverse proportionality between the maximum rate of change of seawater sulfate δ34S and the residence time of sulfur in seawater (cf. Eq. B0).

Second, the reviewer opines that "this approach is only valid if the rate of change is equal to the residence time of the respective system." We agree that the rate method yields an accurate estimate of seawater sulfate concentrations only if FPY is parameterized in a manner consistent with t, which basically requires the system to be in equilibrium. If a value for FPY is chosen that is much larger or smaller than the true equilibrium flux, then seawater sulfate concentrations will be overestimated or underestimated, respectively. We consider these issues further in our reply to the next comment.

Action: We have added a brief mention of these issues to the text of the manuscript and an extended discussion as Appendix B of the revised manuscript. We did not insert this material into the text as it is of tangential importance to the development of the main theme of our paper.

This brings me to my main concern with this model. Equation 3 relates the rate of change to the marine sulfate concentration using a time invariant pyrite burial flux. However, the pyrite burial flux itself depends on the marine sulfate concentration. This dependency is weak above 12mM, but becomes significant for lower concentrations. While the exact relation is not known, and probably changes through time, Wortmann and Chernyavsky (2007) provide a useable parametrization in their supplemental data. This point requires attention before the MS can be published.

Response: The reviewer has raised an excellent point. We agree that the pyrite burial flux has almost certainly varied through time. Since pyrite burial flux is a component of Equations 2 and 3, variations in this parameter will influence calculated seawater sulfate concentrations. Thus, it would be desirable to parameterize such variation in our rate method.

First, we explored the effects of varying pyrite burial fluxes on seawater sulfate estimates as follows. Equations 2-3 of Algeo et al. (2014) have four variables: [SO42-]SW (or MSW, since these are inter-convertible via Equation 4), FPY, D34SCAS-PY, and $\partial\delta34SSO4/\partial t$. However, D34SCAS-PY can be modeled as a function of [SO42-]SW (i.e., the MSR trend of Figure 2 and Equation 6), reducing the number of potentially independent variables to three (we state "potentially independent" as there may in fact be some dependency among these variables). Now it is possible to explore the effects of simultaneous variations in [SO42-]SW and FPY on $\partial\delta34SSO4/\partial t$(max) via a modified form of Equation 2:

$\partial\delta34SCAS/\partial t$(max) = k1 $\times$ k2 $\times$ FPY $\times$ exp(log[SO42-]SW * 0.42 + 1.10) / [SO42-]SW (B5)

The three modeled parameters exhibit log-linear relationships, with larger $\partial\delta34SCAS/\partial t$(max) associated with larger [SO42-]SW and FPY (Fig. B1–see Supplementary document). $\partial\delta34SCAS/\partial t$(max) scales linearly with FPY, so uncertainty in the latter parameter is directly mirrored in the former parameter. In our study (Algeo

et al., 2014), we used fixed estimates of FPY, either 4×10^{13} g yrˆ-1 for oxic oceans or 10×10^{13} g yrˆ-1 for anoxic oceans. This range of FPY values is consistent with variation in $\partial\delta34SCAS/\partial t$(max) from ∼1 to 100 ‰ Myrˆ-1 (Fig. B1âĂŤsee Supplementary document). Wortmann and Chernyavsky (2007) inferred [SO42-]SW-dependency of the pyrite burial flux (their figure 4; red curve, Fig. B1âĂŤsee Supplementary document). If correct, this relationship indicates that variation in $\partial\delta34SCAS/\partial t$(max) cannot exceed ∼3 ‰ Myrˆ-1 under any set of conditions. This result is at odds with numerous well-documented examples of higher rates of $\delta34SCAS$ variation in paleomarine sedimentary units (e.g., Algeo et al., 2014, Table A4).

As noted by the reviewer, variable pyrite burial fluxes will certainly have an influence on seawater sulfate concentration estimates. We have tested this influence by applying the relationship between [SO42-]SW and FPY given by Wortmann and Chernyavsky (2007, their figure 4) to our rate-method calculations. Their relationship can be reduced to a logarithmic expression:

FPY = 0.7681 × ln([SO42-]SW) + 1.405 (B6)

where FPY is in units of 10ˆ13 g yrˆ-1 (rather than in mol yrˆ-1, as in their paper) and [SO42-]SW is in units of mM. This expression yielded a r2 of 0.98 in relation to Wortmann and Chernyavsky's curve (their figure 4). In making use of temporally variable pyrite burial fluxes for calculation of seawater sulfate estimates, Equations 3 and 4 of our paper (Algeo et al., 2014) must be reorganized as follows:

[SO42-]SW(max) / FPY = k1 × k2 × D34SCAS-PY / $\partial\delta34SCAS/\partial t$(max) (B7)

Although Equation B7 has two unknowns, i.e., [SO42-]SW(max) and FPY, it can be solved because FPY is a function of [SO42-]SW in figure 4 of Wortmann and Chernyavsky (2007). The empirical relationship between [SO42-]SW and [SO42-]SW(max) / FPY derived from that figure is given by the polynomial equation:

[SO42-]SW(max) / FPY = -0.0018([SO42-]SW)2 + 0.2842([SO42-]SW) + 0.4651 (B8)

With substitution and reorganization, Equations B7 and B8 yield:

0 = -0.0018([SO42-]SW)2 + 0.2842([SO42-]SW) + (0.4651 âĂŠ k1 × k2 × D34SCAS-PY/[∂δ34SCAS/∂t(max)]) (B9)

This second-order polynomial equation can now be solved for [SO42-]SW using the quadratic solution, after which FPY can be calculated from Equation B6.

Using Equation B9, we calculated [SO42-]SW on the basis of ∂δ34SCAS/∂t(max) and D34SCAS-PY. These relationships are plotted as variation in ∂δ34SCAS/∂t(max) as a function of [SO42-]SW and D34SCAS-PY (Fig. B2âĂŤsee Supplementary document; cf. Figure 1 of Algeo et al., 2014). At high [SO42-]SW, the two sets of ∂δ34SCAS/∂t(max) curves are nearly co-linear, which is because the value of FPY in figure 4 of Wortmann and Chernyavsky (2007) for [SO42-]SW >10 mM is nearly invariant and similar to the flux that we used (i.e., 4 × 1013 g yrˆ-1). In contrast, the two sets of curves diverge sharply at [SO42-]SW <1 mM, which is a consequence of the much lower FPY values associated with low seawater sulfate concentrations in the Wortmann and Chernyavsky curve.

There are a couple of worthwhile observations to make about the ∂δ34SCAS/∂t(max) curves based on the Wortmann and Chernyavsky (2007) relationship. First, the MSR trend of Algeo et al. (2014) corresponds almost entirely to a limited range of ∂δ34SCAS/∂t(max) values (i.e., 2 to 4; Fig. B2âĂŤsee Supplementary document). This suggests that there ought to be quite limited variation in ∂δ34SCAS/∂t(max) over a wide range of seawater sulfate concentrations in nature. Second, many combinations of the two sediment parameters that can be measured (i.e., D34SCAS-PY and ∂δ34SCAS/∂t(max)) cannot yield a [SO42-]SW estimate. For example, for a D34SCAS-PY value of 7‰ any ∂δ34SCAS/∂t(max) value >4 does not yield an estimate of [SO42-]SW (Fig. B2âĂŤsee Supplementary document). This situation exists because high rates of variation in seawater sulfate δ34S are not possible where the pyrite burial flux is sharply curtailed by [SO42-]SW-dependency (as in figure 4 of Wortmann

and Chernyavsky, 2007). However, many paleomarine units exhibit $\partial\delta34SCAS/\partial t$(max) values outside the narrow range permitted by the Wortmann and Chernyavsky (2007) relationship (see Table A4 and Figures 6-8 of Algeo et al., 2014).

What conclusions can be reached from this analysis? Use of [SO42-]SW-dependent values of FPY allows no $\partial\delta34SCAS/\partial t$(max) values greater than $\sim$3 ‰ Myrˆ-1 under any set of conditions, which is at odds with the results of numerous published studies. If the Wortmann and Chernyavsky (2007) parameterization of the FPY-[SO42-]SW relationship is correct, then one must conclude either that all of these published higher rates are products of uncertain geochronologic dating, diagenetic artifacts, or sample processing and analytical problems. This seems inherently unlikely. On the other hand, use of fixed values for FPY in the rate-method calculations of Algeo et al. (2014) yields estimates of [SO42-]SW that areâĂŤfor the most partâĂŤconsistent with estimates of [SO42-]SW based on the MSR-trend method (see Figures 6-8 of Algeo et al., 2014, for examples). The consistency of results for these two quasi-independent methods thus provides a degree of confidence in their validity. Does this mean perforce that pyrite burial fluxes are not dependent on seawater sulfate concentrations? Not necessarilyâĂŤsome form of [SO42-]SW-dependency may exist, but perhaps the form of this dependency is different from that given in Wortmann and Chernyavsky (2007).

Action: We have added a brief mention of these issues to the text of the manuscript and an extended discussion as Appendix B of the revised manuscript. We did not insert this material into the text as it is of tangential importance to the development of the main theme of our paper.

We also calculated paleoseawater sulfate concentrations using [SO42-]SW-dependent pyrite burial fluxes. For the rate-method estimates of Phanerozoic [SO42-]SW given in Figure 4 and Table A3 of Algeo et al. (2014), this procedure yields [SO42-]SW estimates that are close to ($\pm$10%) our original values. This result was obtained because the $\partial\delta34SCAS/\partial t$(max) values of the Phanerozoic record are almost uniformly low (<3 ‰ Myrˆ-1; Figure 3b of Algeo et al., 2014), which is mainly a consequence of

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data smoothing in constructing the Phanerozoic curve (see discussion in Algeo et al., 2014). At such low $\partial\delta34SCAS/\partial t(max)$ values, there is little difference in the [SO42-]SW estimates generated with and without [SO42-]SW-dependent pyrite burial fluxes (see Fig. B2âĂŤsee Supplementary document). For the intervals of high-frequency $\delta34SCAS$ variation shown in Figures 6-8 and Table A4 of Algeo et al. (2014), many units have combinations of D34SCAS-PY and $\partial\delta34SCAS/\partial t(max)$ values that cannot yield an estimate of [SO42-]SW per the Wortmann and Chernyavsky (2007) relationship.

In their second approach, the authors provide an empirical relationship between sulfate concentration and the difference between the S-isotope ratios measured from sulfate and pyrite. This is intriguing but it remains unclear to me how reliable this proxy is, because we have not enough data to check their results against (Fig. 5 insinuates to much here, as the majority of the data shown there is not primary, but proxy data). I am particularly concerned about the mismatch between the authors data and the reconstructions by Wortmann and Paytan (2012). Granted, the latter paper is controversial, however the Cretaceous to Eocene interval is the one time in Earth history where we have large and fast S-isotope variations, a highly resolved marine S-isotope record, and fluid inclusion data which suggest sulfate concentration changes on the order of 20 mM. So this requires special attention.

Response: The first point relates to whether mineral sulfide $\delta34S$ is an adequate proxy for aqueous sulfide $\delta34S$ in developing the MSR trend (Figure 2 of Algeo et al., 2014). We have already addressed this point at length in our paper (see second paragraph of Section 2.2), considering S-isotopic fractionations between aqueous sulfide and mineral sulfide. One point that bears reflection is that estimates of paleoseawater [SO42-]SW are based not on aqueous sulfide $\delta34S$, which cannot be measured for paleo-marine systems, but on mineral sulfide (generally pyrite) $\delta34S$. Therefore, the critical relationship for establishing a viable MSR-trend proxy for [SO42-]SW is that between sulfate $\delta34S$ and mineral sulfide $\delta34S$.

The second point claims a mismatch between our data and that of Wortmann and Paytan (2012). We presume that the reviewer is referring to the differences in [SO_4^{2-}]SW estimates for the $\sim$120 to 50 Ma interval, during which the estimates of Wortmann and Paytan (2012) are uniformly <7 mM (their figure 2b) whereas those of Algeo et al. (2014) are $\sim$13-16 mM (with an uncertainty range of ca. 2X; Figure 4). We agree that there are modest differences in absolute [SO_4^{2-}]SW estimates between these records, although the 120-50-Ma interval is one of low seawater sulfate concentrations (relative to the preceding and following intervals) in both studies, so there is significant agreement in that regard. The absolute values of the Phanerozoic [SO_4^{2-}]SW curve in Figure 4 of Algeo et al. (2014) are a function of the input dataset, which is the Phanerozoic D34SCAS-PY record of Wu et al. (2010). The latter is a large compilative dataset that perforce entailed considerable data averaging, which is likely to have dampened the range of variation in the long-term trend. If so, it is possible that the lower [SO_4^{2-}]SW estimates for the 120-50-Ma interval of Wortmann and Paytan (2012) are more accurate. However, the fact that we have used a somewhat smoothed input dataset in calculating a Phanerozoic [SO_4^{2-}]SW curve does not comment in any way on the validity of the D34SCAS-PY-[SO_4^{2-}]SW relationship (i.e., the MSR trend) in our paper (Algeo et al., 2014, Figure 2).

Action: We have added a brief discussion of these issues to the revised manuscript.

If I understand the authors correctly, they argue: A) that the current $\delta34S$ record could be a local record in the Tethys basin. However a significant part of the Cretaceous $\delta34S$ data is from Site 305 (Shatsky Rise, W-Pacific) and fits nicely with the data from Site 766 (Indian Ocean, possibly restricted); B) that their model may not capture short term draw down events. If so, two questions come to mind: A) Even if the draw down may be short term, the recovery will take a very long time. Using modern fluxes, Wortmann and Paytan (2012) estimate that it takes 60 Million years for the sulfate concentration to recover. If the Algeo et al. model is indeed insensitive to "short term" draw down events, short term events will introduce considerable error in their reconstructions. B)

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More importantly however, why would be a sulfate-pyrite difference model like the one proposed here, be insensitive to short term draw down?

Response: Regarding the possible influence of restricted watermasses, we offered the hypothesis that the unusually low rate-based $[SO_4^{2-}]_{SW}$ estimates of a subset of the Mesozoic units shown in Figure 8 of Algeo et al. (2014) may have been due to watermass restriction. The units in question (labeled r, t, t', v, and w in Figure 8) were located in the north-central Tethys (Tibet), western Tethys (England), South Atlantic, and North American Western Interior Seaway. A case can be made for some degree of watermass restriction in each area, although this remains a hypothesis, and it is possible that additional S-isotopic work might upwardly revise the rate-based $[SO_4^{2-}]_{SW}$ estimates for these units. We do not believe that these findings conflict with the results of Wortmann and Paytan (2012).

Regarding the rate of recovery of seawater sulfate concentrations, Wortmann and Paytan (2012) infer a recovery interval of ∼60 Myr following a 120-Ma drawdown event. However, the mathematics of reservoir theory shows that recovery intervals should be of similar duration to the residence time of a given seawater component, which is ∼13 Myr for seawater sulfate at present and would be shorter if the recovery "target" concentration were lower. Other factors must have contributed to the extended recovery interval observed by Wortmann and Paytan (2012).

Regarding the insensitivity of our model to short-term seawater sulfate drawdown, this is a function of the input dataset, which is the Phanerozoic D34SCAS-PY record of Wu et al. (2010), and not of the MSR-trend method of estimating paleoseawater $[SO_4^{2-}]_{SW}$. The Wu et al. record is a large compilative dataset that perforce entailed considerable data averaging, which is likely to have dampened the range of variation in the long-term trend and reduced or eliminated short-term events. The Phanerozoic $[SO_4^{2-}]_{SW}$ curve that we generated from this record (Fig. 4 of Algeo et al., 2014) should be regarded as representative of long-term seawater sulfate trends but without short-term drawdown events. This interpretation is reinforced by comparison of our

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Phanerozoic [SO42-]SW curve with estimates based on other techniques (Fig. 5 of Algeo et al., 2014). The MSR-trend method of estimating paleoseawater [SO42-]SW is certainly capable of capturing short-term drawdown events, provided that these events are present in the D34SCAS-PY record that is used as input data for [SO42-]SW calculations.

Action: We have added a brief discussion of these issues to the revised manuscript.

Specific Comments

1. p13188 l10, and p 13192 l10. The rate of change is not only determined by reducing the input/output flows to zero. You could also double or triple those flows, which would have a considerable effect on the rate of change. Or is this an oblique way to state that the model is only valid if the rate of change is equal to the residence time?

Response: This question was fully addressed above.

2. p13188 l20 ff and later in the manuscript. I always thought that the Early Triassic sulfate concentrations are low. The rapid changes observed during this time certainly require sulfate concentrations below 10 mM (e.g. Song et al., 2014)?

Response: We agree, and this point is addressed specifically on p13188 l22-24 and later in the paper.

3. p13188 l23 What is the meaning of "varied only slightly since 250 Ma"? Some of our most reliable data on sulfate concentrations is of Jurassic and Cretaceous age, and even fluid inclusion data suggest pretty dramatic changes from 8 mM during the Early Cretaceous to modern values around 28 mM (Lowenstein et al., 2001, 2003; Demicco et al., 2005).

Response: We cite a range of ∼10-30 mM in the same sentence in which we state "varied only slightly since 250 Ma". Variation over a range of ∼3× is small compared to the much larger variations (probably ∼20-100×) that occurred during the Neoproterozoic and Paleozoic. We cannot go into complex details in the Abstract; more specific

values and ranges are cited later in the paper.

4. p13188 l24 I'd add the Cretaceous here, see above.

Response: OK, done.

5. p 13191 l15 there is a pretty rich literature on the subject, however the paper cited here only discusses data from a lake and lagoon.

Response: Agreed. We have added additional citations.

6. p p 13192 eq 2 Fpyr itself depends on the sulfate concentration (Wortmann and Chernyavsky, 2007). As stated, the equation will only work for concentrations above 12 mM.

Response: This question was fully addressed above.

7. p13193 l20. I seem to remember that the Paytan et al. (1998) data showed faster variations?

Response: In Figure 1a of the Paytan et al. (1998) paper, the intervals of most rapid variation in seawater sulfate are (1) from ~18.0‰ to 21.6‰ at 51.5-45.5 Ma, which represents a change of 3.6‰ in 5.0 Myr, or ~0.7‰ Myr^-1, and (2) from ~22.0‰ to 21.0‰ at 2-0 Ma, which represents a change of 1.0‰ in 2.0 Myr, or ~0.5 Myr^-1. We agree that the maximum observed rate of change in sulfate δ34S is <0.7‰ Myr^-1 and have amended it accordingly. Although this is more accurate, it does not change the basic point that we are makingâĂŤthat the maximum observed rate of change for the Cenozoic is less than the theoretical maximum.

8. p13197 l17. Consider adding the work of Rudnicki et al. (2001).

Response: OK. This paper is now cited.

9. p13197 l27, Canfield and Teske (1996), and their data indicates a spread up to 70 permil.

Response: We stated that MSR fractionation is "typically ∼30 to 60‰ in modern marine systems" and we stand by this statement. We do not deny that more extreme values (both lower and higher) have been reported in some studies.

10. p13198 l25, the works of Rees (1973) and Brunner and Bernasconi (2005) are important here too.

Response: OK. These papers are now cited.

11. p13199 1 para. Since this is a fairly exhaustive list of processes affecting S fractionation, the author may want to consider to add Eckert et al. (2011) who show that cell external sulfide may affect S-fractionation (see also Brunner and Bernasconi, 2005).

Response: OK. This process and a citation to Eckert et al. (2011) have been added.

12. p13201 l 2, add citation for the Lowess model.

Response: The reader is already referred to Song et al. (2014), a study that provides both the algorithms and references to background material on LOWESS estimation. Additional documentation is not needed.

13. p13202 l5ff, p13204, The Song et al. (2014) data suggests that the Permo-Triassic concentrations must have been low?

Response: Yes, and this is discussed on p13206 l27-28 and p13207 l1-3, with data given in Table A4 and illustrated in Figure 8.

14. p13207 l9, Canfield and Teske 1996, and the values reported there seem to go up to 70 permil?

Response: We agree that the natural SRM populations documented by Canfield and Teske (1996) exhibit fractionations up to 70‰ although these populations display a distinct mode at 40-60‰ Our citation of a range of 30-60‰ was based on the average fractionations given in Table A1, so we have deleted the reference to Canfield and Teske (1996) and cited our Table A1. It should also be noted that the 30-60‰ range

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cited here represents typical marine MSR fractionation values, not the full range of reported values in nature (which would be larger).

15. p13207 l20ff If I understand this correctly, the rate based estimate really only works if the rate of change equals the residence time. If it is slower, or faster, this approach will fail. It might be useful to rephrase the discussion in the more general framework of residence time vs, rate of change.

Response: This question was fully addressed above.

16. p13209 l 5ff. I am not sure that I understand this argument. While I can see that the difference between CAS and Pyrite may be affected by the local hydrogeography, the sulfur data published by Paytan et al. (1998) are from coring locations in the Pacific, and as such not affected by local restriction. So the rate method should apply here.

Response: The discussion of South Atlantic paleohydrography on these lines does not refer to the Paytan et al. (1998) dataset but to that of Wortmann and Chernyavsky (2007), which is from a site in the South Atlantic. This paper is cited in the text, but the sources of data in Table A4 were inadvertently left out, which may have confused the reviewer. We have restored the sources of data to Table A4.

17. Last but not least, it would be useful if the authors provide their p-values for their regression model, as the r2-value only describes how good the fit is, but says nothing about how probable the model is.

Response: The r2 values reported here are all high (0.74 to 0.80) and the number of samples large (n = 31 to 81)âĂŤconsequently, the associated alpha errors (p(a)) are all <0.01. We thought that this would be obvious to readers, but we have added p(a) values wherever r2 is reported.

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Please also note the supplement to this comment: http://www.biogeosciences-discuss.net/11/C8285/2015/bgd-11-C8285-2015-supplement.pdf

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