RC2: 'Comment on essd-2023-67'

Christophe Monnin

L. 348 et seq. The criterion for equilibrium cannot be Ω =1.0000000…. which never happens. Instead a range of Ω values must be defined, that reflects the uncertainties in the input data (Ba and SO4 concentrations) and in the thermodynamic model (barite solubility product and activity coefficient). Taking Ω values between 0.9 and 1.1 is already a very demanding criterion that we have retained in our paper (Monnin et al., 199). So the discussion in this paragraph should be corrected according to this. For example Ω = 0.97 can be considered as a sign of barite equilibrium. See Monnin et al., 1999 for a discussion. I see that the authors discuss this point in section 5.2.3.

We thank Christophe Monnin for his important insights, which were also entertaining to read!

This is an interesting point and we've made five changs in response to this comment. First, we note that the values of Ω possess an uncertainty (Sect. 4.2):

"Model #3080 contains 3,302,570 predictions for each of [Ba], Ba*, and Ωbarite (Sect. 6). Assuming that the MAPE and MAE are good estimates of the prediction error, we estimate that modeled [Ba] and Ba* have uncertainties of 6.0 % and 4.3 nmol kg–1, respectively. Uncertainties on Ωbarite were estimated by comparison to literature data, which yields a MAE of 0.08. These estimates are discussed in more detail in Section 5.2 and the Appendix."

Second, also in Section 4.2., we make a similar point when describing the volume-weighted histograms:

"Lastly, Ωbarite tends to increase between the 0–250 m, 250–1,000 m, and 1,000–2,000 m depth bins, increasing from 0.42, to 0.65, and 0.96, respectively. Average Ωbarite in the deepest bin (2,000–5,500 m) is slightly lower, with a mean value of 0.92 (Fig. 9D). Given the accuracy of our model-derived Ωbarite predictions (0.08 to 0.10), the ocean between 1,000–5,500 m is within uncertainty of BaSO4 equilibrium."

Third, we clarify where these uncertainties come from in Section 5.2.3.:

"Given the nature of these uncertainties, we opted to calculate prediction uncertainties for Ωbarite empirically by comparison to literature data (see Appendix). This yields a value between 0.08 and 0.10, similar to the 10 % prediction error reported by Monnin et al. (1999)."

Fourth, we provide these details in the Appendix:

"We can use these comparisons to estimate the prediction uncertainty on our model-derived values of Ωbarite. The MAE of the 133 comparisons shown in Fig. A1 yields a value of 0.10. However, there are different numbers of points in each profile; we thus believe it is more appropriate to average the MAE calculated for each of the five profiles, which yields a value of 0.08. Both values are similar to the 10 % prediction uncertainty reported by Monnin et al. (1999)."

And fifth, we note what this means for assessing equilibrium in Section 5.3.3.:

"By comparison to literature data, we estimate that our model achieves a typical prediction uncertainty on Ωbarite of 0.08 (see Appendix). Accordingly, values of Ωbarite between 0.92–1.08 can be considered as 'BaSO4 saturated,' whereas values of Ωbarite <0.92 or >1.08 indicate under- or super-saturation, respectively."

The updated Figure A1 (with model #3080 output is shown below):

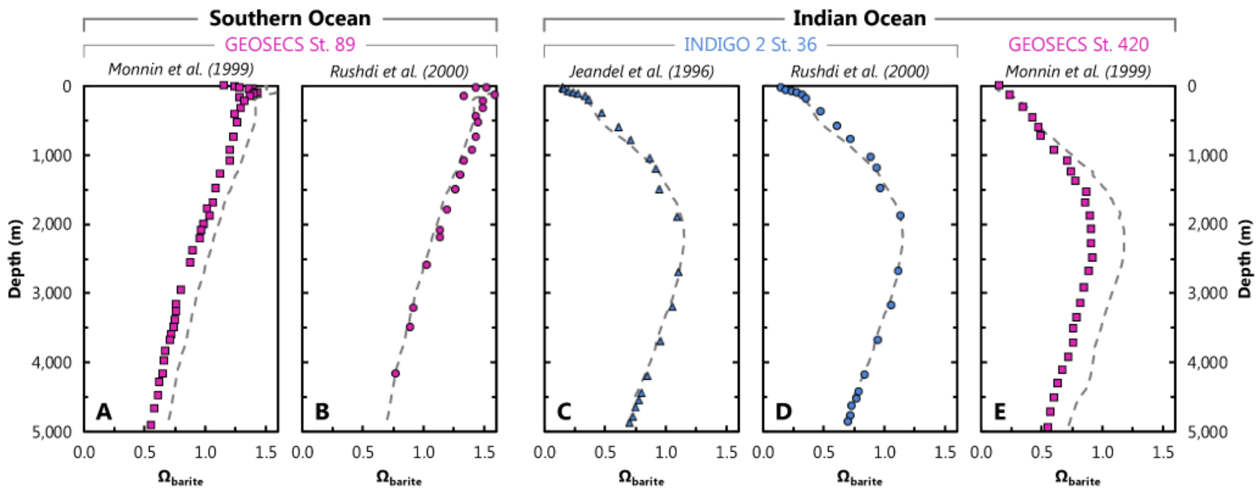

Figure A1. Comparison of literature- (symbols) and Model #3080-derived (dashed line) values of Ω_{barite}. Panels **A** and **B** show profiles of Ω_{barite} at GEOSECS St. 89 (60°0' S, 0°2' E). The other panels are from the Indian Ocean: **C** and **D** are from INDIGO 2 St. 36 (6°9' S, 50°55' E) and **E** from GEOSECS St. 420 (0°3' S, 50°55' E), some ≈675 km north of INDIGO 2 St. 36.

Also the statement in the abstract that "the ocean below 1,000 m is, on average, at or near saturation" is a simplification of what has been previously depicted by Monnin et al. (and by Rushdi et al.). For example we wrote that in the Pacific Ocean "There is a return to undersaturation of the water column at depths of about 3500 m in the Pacific and of about 2500 m in the Southern Ocean. The reverse is found for GEOSECS station 446 in the Gulf of Bengal for which the highest Ba concentrations can be found at depth: surface waters are undersaturated and equilibrium is reached below 2000 m". This simplifying statement by the authors deteriorates the conclusions that they have obtained with their powerful and elaborate approach.

Fair enough! We've addressed this point in two ways. First, we note in Section 5.3.3. that earlier studies already discerned the major contours in the global distribution of Ω:

"Global patterns in Ωbarite derived using our model are similar to those reported by Monnin et al. (1999) and Rushdi et al. (2000). Readers looking for detailed basin-by-basin descriptions of Ωbarite are directed to those studies."

Second, we added a caveat in the abstract stating that there are regional variations in Ω:

“We also calculate the saturation state of seawater with respect to barite. In addition to revealing systematic spatial and vertical variations, our results show that the ocean below 1,000 m is at equilibrium with respect to barite.”

The discussion averaging barite saturation for the global ocean (L. 579-580:" the ocean below 1,000 m exhibits a mean Ω barite ≥0.92, which implies that much of the deep ocean is close to saturation with respect to $BaSO_4$") tends to hide the fact that specific regions of the global ocean do not fit in this picture and should be given close attention (e.g. the role of hydrothermal activity above ridges, or, as discussed by the authors, the continental input through river discharge).

We opted to avoid discussing detailed regional patterns in Ω as the reviewer rightly notes that this has been tackled by previous studies. (Conversely, no such discussion of global variability in Ba* exists, and we took the opportunity provided by Reviewer #1 to address this issue.) In response to this point, we tried to make it clearer that our focus, with respect to Ω, was on three main things: (i) accuracy of our Ω estimates, (ii) whether our values reproduce known features in Ω, and (iii) the global mean Ω. The following text now appears as the preamble to Section 5.3.3.:

“Here we show that our approach can predict Ωbarite with an MAE of 0.08, that our output is in agreement with published values, and that the deep ocean, below 1,000 m, is at saturation with respect to $BaSO_4$.”

This being said, the paper is quite well organized, the presentation of the model and of the results quite concise.

Excellent!

No changes made.

Although my opinion is that the discussion repeats in part what has been concluded from what the authors call mechanistic models and as such should be simplified, the paper presents a very good account of the Ba problem in the ocean and a way to address it (by what could be called "brute force"…). It could be published as it is. The fact that the model can be adapted for other tracers with a minimal effort is quite encouraging.

Excellent – thank you! We may even borrow some of this language for use in future presentations: “Barium by brute force: Results from an ML model”

No changes made.

L. 67: missing figure number

Added cross reference to Figure 1.

Typo in the vertical axis of Fig. 4, 5 and 6D: replace the lower 1.75 by 0.75.

Changed.

L.338. Sentence construction inadequate.

Good catch. The revised sentence reads:

"Based on our formulation (Eqs. 1, 2), Ba* varies from –27.2 to +27.9 nmol kg–1 and possesses an unweighted mean of +2.4 nmol kg–1."