

## ***Interactive comment on “Biogeochemistry of manganese in Lake Matano, Indonesia” by C. Jones et al.***

**C. Jones et al.**

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BG 2011-118 Response to Reviews

First, we would like to express our appreciation to the referees for two constructive and insightful reviews.

We respond to comments from anonymous referee 1 followed by those of anonymous referee 2.

Referee 1:

1. Since both reviewers found issue with our assertion that Mn oxidation rates in diverse environments displayed marked similarity, we have removed this paragraph and the

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corresponding table.

2. We feel that the possibility of anaerobic methane oxidation coupled to Fe and Mn oxide reduction in Lake Matano is highly relevant to this discussion, as this process could be a significant sink for Mn oxides and therefore relevant for the study of Mn biogeochemical cycling. We have, however, reworded the section to read, “Recent studies, including one at Lake Matano, have linked biological Mn (and Fe) oxide reduction to methane oxidation (Beal et al., 2009; Crowe et al., 2011). Lake Matano provides some of the most compelling evidence to date of CH<sub>4</sub> oxidation coupled to Fe/Mn oxide reduction given the dearth of both SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in the lake.”

3. The terminology referred to by the reviewer (4, 4074) now reads, “This suggests the formation of a Mn species that is not reactive to the selective extractions described above. This Mn species, however, like other oxidized forms of Mn, is subsequently dissolved by reduction as it sinks through the water column (see below).” To clarify any confusion, we have also changed (11-12, 4080) to read, “Based on the distribution and oxidation state of Mn particles (Figs 3 and 5), Mn oxides are formed near the chemocline and reduced in the water column by 120.5 m.”

4. The total source of Mn to the deep lake is represented in the model as an epilimnetic vertical flux. Effectively, it represents both the vertical (by particle settling and diffusion) and lateral (by sediment slumping) fluxes of Mn. The impossibility of adequately representing lateral fluxes in a 1D model results in a higher-than-observed epilimnetic concentration of particulate Mn, as discussed in the text. Regardless of the lateral versus vertical source, the fluxes away from the Mn(II) concentration peak and the corresponding transformation rates are still valid. This has been reiterated in the text.

5. The sentence was changed to accommodate the reviewer's suggestion.

6. The sentence was changed to accommodate the reviewer's suggestion.

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7. We have added, “where concentration gradients were calculated as the slope of a linear regression computed for depth versus concentration at each given depth interval,” to the text describing equation 1, and we have added the relevant depth intervals to Table 7.

8. (5, 4082) “overlying waters” has been changed to “water immediately overlying the sediments”.

9. Anoxic bottom waters lacking strong reductants like Fe(II) and HS<sup>-</sup> would not preclude Mn oxide deposition. This is the basis for our conceptual model of the manganous ocean and sedimentary Mn enrichments that may punctuate ferruginous to sulfidic transitional periods.

10. In the second scenario, the waters immediately overlying the sediments are not anoxic; a similar scenario for Mn deposition has been described previously by Calvert and Pedersen (1996). The kinetics of Mn(II) oxidation are much slower than Fe(II) or sulfide oxidation, thus Mn(II) (regardless of source, but feasibly from hydrothermal vents) could persist and accumulate in a water column with low oxygen concentrations.

11. Figure 8b caption now reads, “b) Natural log of Mn(II) concentration versus time from 119-121 m, demonstrating the applicability of first order reaction kinetics in Lake Matano.”

Referee 2:

1. We have included stronger emphasis on the utility of the lake as an analogue for Precambrian ocean biogeochemistry. To the title, we have also added the adjective ‘ferruginous’ before ‘Lake Matano’ for emphasis.

2. To clarify, no particulate Mn was detected just below the peak in particulate Mn, and a corresponding increase in Mn(II) is seen in this zone. Water column particles were not sampled in the deep waters (below 130 m), and the cause of the drawdown in Mn(II) in these deep waters is assumed to be precipitation of a Mn(II) bearing mineral.

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We based the identification of this mineral as pseudo kutnahorite on saturation indices calculated for the bottom waters. Additionally, since these bottom waters are very well mixed, we do not specify that the mineral forms in the water column, only that, “Mn is likely sequestered in these sediments as pseudo kutnahorite.”

3. The sentence, “The addition of Mn(II) up to 40  $\mu\text{mol l}^{-1}$  is a 2.5 to 7 fold increase of ambient Mn(II) concentrations depending on depth and could cause artifacts in the incubations, e.g. microbial community changes, mineral property changes because of increased Mn(II) surface sorption, and saturation of Mn oxidizing enzymes,” has been added to the methods describing the Mn oxidation rate incubations.

4. At the reviewer’s suggestion, we have calculated rates based on the first two time points. We have added to the explanation for slow rate observation the following, “The long incubation times and higher than ambient Mn(II) concentrations, however, may have produced artifacts in our rate observations. Recalculating Mn oxidation rates based only on the first two time points for 119 - 121 m gives higher rates of 0.36 -0.72  $\mu\text{mol l}^{-1}\text{d}^{-1}$ . The higher Mn(II) concentrations may have led to saturation of cell surfaces and enzymes by Mn oxides, further lowering the Mn oxidation rate. Alternatively, sorption of Mn(II) onto the Mn oxides produced could lead to the calculation of Mn oxidation rates that are higher than the in situ rates, since the rates are calculated based on the change in Mn(II) concentration over time.”

5. Using a linear combination analysis of Mn(II), (III), and (IV) standards with our water column particle oxidation state data showed less than 10% contribution from Mn(II)/(III), which is within the error of the analysis. To address the reviewers comments, in the discussion of XANES particulate Mn oxidation states, we have added the following statement: “We find no evidence for a significant Mn(II) contribution, implying that sorption to particles is not a major sink for Mn(II) in this environment.”

6. As mentioned in the response to the first reviewer, we have removed this paragraph and table.

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7. We have edited the relevant section for clarity. It now reads, “Assuming pseudo-steady state, the rate of Mn leaving the water column must equal the rate of Mn input. Thus, we can equate the downward flux of Mn(II) (driven by Mn(II) mineral precipitation/sedimentation),  $61 \mu\text{mol m}^{-2} \text{d}^{-1}$  (Table 7), with the total flux of Mn into the system. We assume Mn enters the system in oxidized form. Since Mn leaves the water column as a Mn(II) mineral, all the oxidized Mn must ultimately be reduced. Mn reduction can then be calculated as the sum of the upward (oxidative) and downward (precipitation driven, which is equal to the oxidized Mn input) fluxes ( $821 + 61 = 882 \mu\text{mol m}^{-2} \text{d}^{-1}$ ).

8. The significance of the mineralogy results was expanded to include studies from marine environments and laboratory cultures. The sentence now reads, “The dominant Mn mineralogy at 118.6 m appears, therefore, to be birnessite, consistent with previous studies of biological Mn oxidation products in lake environments, as well as in marine and laboratory culture studies (e.g. Friedl et al., 1997; Dick et al., 2009; Villalobos et al., 2003).”

9. The reviewers concerns are noted, and along with the discussion of environmental rate constants for Mn oxidation, this discussion has been removed.

10. This has been removed.

Technical corrections:

1. This is corrected.

2. There is a detail of the chemocline in figure 3 (bottom panels) showing  $\text{O}_2$ , dissolved Fe and Mn, and particulate Fe and Mn.

3. The figure (attached) has been amended to show a box delineating the inset boundaries on the density plot.

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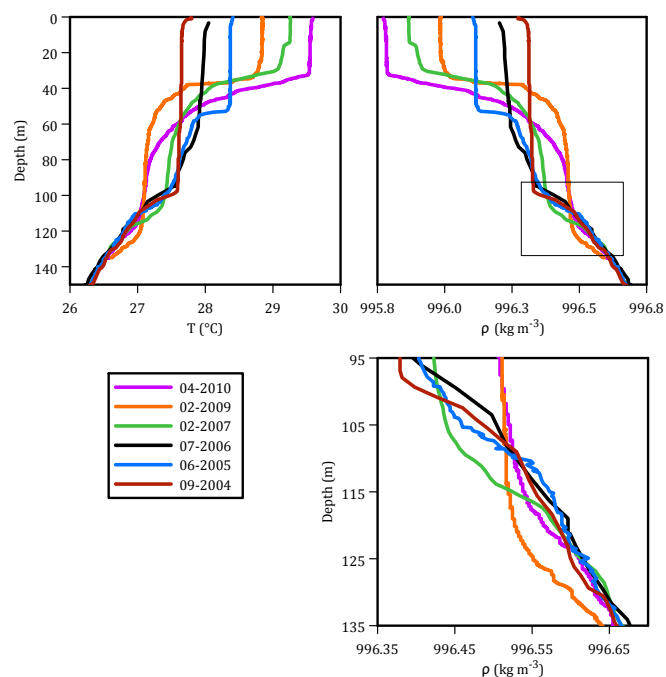


Fig. 1.

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