Metal-Rich Layers in Pelagic Sediments

T. R. S. Wilson et al. (1) present a model that predicts the depth and thickness of metal-rich layers in marine sediments. Reactions of the downward flux of oxidants (O₂, NO₃⁻) in pore waters with reduced solid phases in the sediments (organic and inorganic) and with the upward diffusive flux of dissolved reductants (Fe²⁺, Mn²⁺) are modeled to predict (i) the rate at which redox fronts migrate downward into sediments, (ii) the depth in the sediments at which layers enriched in oxides of Fe and Mn are formed, and (iii) the length of time since deposition of turbidite layers in certain cases.

Essential components of the model include the reaction of dissolved O₂ with dissolved Fe²⁺ and Mn²⁺. However, the chemical equations for these reactions given by Wilson et al. are not stoichiometrically balanced. In their table 1, equation 3 is written as

\[ 4 \text{Fe}^{2+} + 3 \text{O}_2 + 2 \text{H}_2\text{O} = 4 \text{FeOOH} \]

The correct equation is

\[ 4 \text{Fe}^{2+} + \text{O}_2 + 6 \text{H}_2\text{O} = 4 \text{FeOOH} + 8 \text{H}^+ \]

Their equation 4 is written as

\[ 3 \text{Mn}^{2+} + 2 \text{O}_2 = \text{Mn}_3\text{O}_4 \]

The correct equation for precipitation of Mn₃O₄ is

\[ 3 \text{Mn}^{2+} + \frac{3}{2} \text{O}_2 + 3 \text{H}_2\text{O} = \text{Mn}_3\text{O}_4 + 6 \text{H}^+ \]

Correctly balanced, the Fe²⁺/O₂ and Mn²⁺/O₂ molar ratios are 4 to 1 and 6 to 1, respectively, much larger than the ratios of 4 to 3 and 3 to 2 used by Wilson et al. in their model.

As a consequence of using these incorrect ratios, the model of Wilson et al. will (i) underestimate the rate of downward migration of the redox front, (ii) underestimate the depth of the redox front below the sediment-water interface when the downward migration of the front ceases, that is, the depth of the metal-rich layer, and (iii) overestimate the portion of total O₂ consumed attributable to oxidation of Fe²⁺ and Mn²⁺ (that is, underestimate O₂ consumption by oxidation of organic carbon and inorganic solid-phase reduced species).

Given the serious errors in reaction stoichiometries incorporated into the model, it is curious that model predictions can be made to match so well with the observed sedimentary profiles.

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REFERENCES
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Response: Anderson and Schiff (1) are correct in challenging two equations used in our report (2) since neither equation conserves charge. If hausmannite and goethite are the minerals formed (itself an assumption), their suggested stoichiometries are closer to reality than those represented by equations 3 and 4 in our original report.

Anderson and Schiff are incorrect, however, in their implication that this criticism undermines the report in any significant way, as they appear to misinterpret the relative importance of the various processes modeled. The main purpose of the model we developed (2) was to test the concept that a downward propagating oxidation front could form metal-rich layers in the available time, the inputs being "reasonable" parameters culled from the literature and from our own data. In fact, as is clear from the values quoted in the report, the gross behavior of the model is determined by the oxidation of solid-phase organic carbon at the front. In this context, the oxidation of Fe(II) and of Mn(II) is of minor quantitative importance.

To illustrate this point, we have rerun the model with the amendments suggested by Anderson and Schiff. For the Madeira Abyssal Plain station discussed, the estimated age of the turbidite changes from 217 years to 214 years. For the equatorial Atlantic base case the result is an increase of 5.3 cm in the depth of the iron maximum, from 55.6 cm to 60.9 cm. A consequent slight broadening of the peak results in a drop in the maximum Fe₂O₃ enrichment, from 5% to 3%. As the upward diffusional fluxes of the metals are unaltered, the integrated quantities of iron and of manganese oxidized during the 11,000-year run time remained unchanged.

Figure 2 of our original report (2) shows the range of the field data and the effects of various changes in the base case assumptions. Comparison shows that the results quoted above are well within the overall ranges of uncertainty presented in that figure. There is thus no need to revise the important conclusion of the modeling exercise, which is that the propagating oxidation front mechanism described is capable of producing iron enrichments of the type observed in sediments. These enrichments were previously unexplained.

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