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Comment

What controls dissolved iron concentrations in the world ocean? — a comment

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1. Introduction

It is a pleasure to see the high-quality Moss Landing iron data set put together into one place by Johnson et al., with new data included along with the compiled published data. This paper will be an invaluable resource for those concerned with iron in the ocean and its consequences. The Moss Landing data compares well with less extensive data from at least four other labs; it appears that the community begins to agree on the distribution of iron in the ocean. The paper is a fitting memorial to John Martin who assembled this fine team and inspired their efforts. The authors of the paper deserve credit for their substantial work at sea and in the laboratory and for taking on the labor of assembling and interpreting the data set.

Many of the particulars of the paper can be similarly lauded, but the purpose of marine chemistry discussions is not to praise Caesar, but rather to illuminate through critical commentary and reply. So this discussion will focus upon the following three points:

(1) The iron distribution in the deep ocean is less well understood than Johnson et al. imply.

(2) The evidence presented here does not prove that the supply of iron to the open ocean is not predominantly eolian.

(3) The vertical diffusive model for iron in the thermocline and the curve fits are misleading.

Focusing on these points in relation to the great achievement represented by the paper may resemble swatting gnats on the back of a lion. Nonetheless, here I go (roar!).

2. Distribution of iron in the deep ocean

Johnson et al. show that iron has an unusual oceanic distribution. But I believe that they overemphasize the constancy of deep water iron, because data is most lacking in places where it is most likely to differ from the sites included here. Nonetheless, the relative constancy between the oceans, compared to other trace metals which show large gradients, is interesting. Johnson et al. suggest that this constancy may be either set by iron oxide solubility (a difficultto-constrain number) or determined by a strong iron chelator that is uniformly distributed within the deep ocean. These ideas are arguable and are suitable as hypotheses to be tested, but I do not favor either of them.

As counter-example to these ideas for iron, consider the concentration of 230 Th in the ocean. A comparable quantity of data exists for 230 Th as for iron. For the sake of discussion, only two data sets from the Atlantic and Pacific are shown (Bacon and Anderson, 1982; Cochran et al., 1987). Although these data sets do not adequately characterize existing knowledge about the distribution of 230 Th in the

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ocean, these data serve to illustrate that the concentration of ²³⁰Th in the deep ocean is similar in the major ocean basins, just as Fig. 2 of Johnson et al. shows for iron. In contrast to the model of Johnson et al. for iron, no one has suggested that ²³⁰Th solubility or a ²³⁰Th-specific chelator is responsible for this aspect of ocean chemistry. Bacon and Anderson (1982) argue instead that the distribution of ²³⁰Th in the water column is governed by a balance between steady production of ²³⁰Th everywhere in the water column with a steady rain of ²³⁰Th-exchanging particles. Dissolved ²³⁰Th concentrations in the deep water are higher because the particulate flux of ²³⁰Th must increase linearly with depth to reflect the integrated production. The two oceans are similar because the 230 Th residence time is short (30 + 10 yr, according to Bacon and Anderson (1982)) and hence ²³⁰ Th supplies are localized and no inter-ocean transport and accumulation occurs.

There are many points of similarity (and some key differences) between iron and ²³⁰Th. Both elements are strongly scavenged and have short oceanic residence times. The ²³⁰Th residence time is known well because the supply from radioactive decay is known exactly and the ²³⁰Th concentration throughout the ocean is known reasonably well. The iron residence time is known more poorly because the supply rate of iron to the ocean is poorly constrained. Published estimates range from 100-200 years, which is short enough to preclude significant inter-ocean transport (as for 230 Th). One key difference between ²³⁰Th and iron is the uniform generation of ²³⁰Th throughout the water column, as opposed to the much more variable supply of iron to the ocean from eolian deposition, diffusive releases from reducing bottom sediments and the release of dissolved iron during the decay of particulate organic matter (which is concentrated in the upper ocean and leads to iron-nutrient correlations in the upper water column).

The low deep iron concentrations (< 0.5 nmol/kg from the surface to at least 2000 m) observed in the station closest to the South Pacific (3° S; see Fig. 7 of Johnson et al.) are proof that the solubility and/or chelator ideas cannot apply everywhere in the ocean. I suggest that the low atmospheric dust flux in the south Pacific (Fig. 1) is likely to result in low iron concentrations in the deep waters of the south Pacific



Fig. 1. Dissolved ²³⁰Th profiles from the eastern Pacific and western North Atlantic.

and that if more stations were available from the south Pacific Ocean, the 'magic' 0.6 nmol/kg would not apply there. Johnson et al. argue against the role of atmospheric dust as the dominant control on the iron supply to the deep ocean, however, so I move onto the next item.

3. Does the water column inventory of Fe reflect eolian fluxes to the surface ocean?

Bruland et al. (1994) suggested that the water column inventory of Fe was controlled by a balance between the release from eolian dusts in the surface ocean, release through the water column by the decomposition of sinking organic particles) and scavenging of iron onto refractory sinking particles. In their Fig. 10, Johnson et al. plot the 0-500 m inventory of iron against the estimated eolian iron flux for their stations and suggest that there is only a weak relationship at best.

I argue that this comparison of eolian iron fluxes with upper 500 m inventories is problematical. First, strong iron fluxes out of the continental boundaries will mask eolian input for stations influenced by this edge effect (see their fig. 7). Stations from this region ought to be excluded from the comparison. Second, atmospheric dust fluxes show a strong order of magnitude lateral gradients (see their fig. 1), significant lateral transport will occur within the ocean for iron during its 100–200 year residence time. Horizontal mixing within the thermocline will move iron away from its strongest eolian sources into regions with weaker eolian sources. A stationby-station comparison of the local dust flux with water column iron is misleading; the comparison must be done by averaging the eolian iron flux over a larger region. Fig. 10 of Johnson et al. does not rule role o f th e out th e eolian/regeneration/scavenging balance as the principle control on oceanic water column iron inventories and a more elaborate examination will be necessary to assess the concept.

4. Can a vertical-diffusion-only model account for the distribution of iron in the upper ocean?

The authors model the distribution of iron in the upper water column with a simple model whose physics are described by a simple constant vertical diffusion coefficient. If taken seriously, this model could set back chemical modeling in the thermocline by decades.

I realize that all models, especially geochemical models, are simplifications and that it is all too easy to take cheap shots against them for being too simple. For example, the standard Munk/Craig (Munk, 1966; Craig, 1969) vertical advection/diffusion ('vertical A/D') model could be criticized because careful measurements of the rate of internal mixing in the ocean (Ledwell et al., 1993) show that vertical mixing in the oceanic interior may occur 10-100 times more slowly than the model supposes. Even acknowledging the validity of that criticism, however, one could defend the diffusivity required by a vertical A/D model as the end result of an effective vertical diffusivity created by localized mixing (Polzin et al., 1997) and lateral homogenization. It is understood that simple models (perhaps even all models) of the ocean must incorporate a 'parameterization' of 'sub-grid-scale' processes and that the vertical A/D model simply treats the net effect of localized mixing and lateral diffusion within a basin as a 'sub-grid-scale' process that can be approximated by a constant vertical mixing coefficient. Although the vertical A/D model of the deep ocean may not be correct in terms of true local vertical diffusivities, reaction rates estimated from that model



Fig. 2. Communication time of thermocline waters as a function of depth as estimated by vertical diffusivity model and contrasted to the ${}^{3}\text{He}/{}^{3}\text{H}$ estimates of Jenkins (1980).

may well still be correct when they are understood as averages throughout a horizontally-distributed slab.

My criticism of the vertical diffusive model of the thermocline is not directed at it's simplicity, but rather because it clearly mis-estimates rates of transport between the surface ocean and thermocline. A constant-with-depth diffusion-only model of the thermocline would predict, among other things, a temperature gradient in the thermocline that is linear with depth (obviously incorrect). Even worse, it predicts a rate of communication of the upper ocean with the thermocline that is too slow. As an illustration of this principle let us apply the principle that in one-dimensional diffusive situations,

$\overline{x^2} \sim Dt$

where $\overline{x^2}$ is the mean squared distance diffused, D is the diffusion coefficient and t is the elapsed time. The consequences of this model for transport into the thermocline are shown in Fig. 2 and compared with the 3 He/ 3 H-based ventilation estimates by Jenkins (1980) for the subtropical Atlantic near Bermuda. It can be seen that the $1 \text{ cm}^2/\text{s}$ diffusive model underestimates ventilation throughout the thermocline, particularly below 1000 m. The comparison in the upper thermocline could be improved by using $2 \text{ cm}^2/\text{s}$, but the mismatch below 1000 m remains. These differences in ventilation times will result in proportional differences in oxygen utilization rates and accumulated iron regeneration. The vertical diffusive model not only predicts an incorrect distribution of simple physical properties such as temperature and salinity, but it also predicts an erroneous time scale for chemical fluxes within the thermocline. The actual values for ventilation times will of course vary throughout the ocean (upper Pacific ventilation being slower than in the North Atlantic).

Johnson et al. comment on how well some of the data are fit by their model. A successful curve fit should never be mistaken for proof. Given enough degrees of freedom and a suitably flexible function, almost any data set can be fit. Any function that has some curvature relative to depth could fit the iron data no matter what the physical basis of the model. In this case, we know that the physical basis of a vertical-diffusion-only model is incorrect.

Tracer studies demonstrate that vertical diffusivity is lower than $0.1 \text{ cm}^2/\text{s}$ in the thermocline. The best simple chemical model of the thermocline is the Jenkins (1980) outcrop-density-surface box model [a similar model was later applied to ²²⁸Ra by Sarmiento et al. (1990)]. Such a model can allow for reasonable T and S distributions and can account for the penetration of transient and steady-state tracers such as ³H and ²²⁸Ra remarkably well. The model is simple enough that it need not complicate the life of geochemists. The assumptions employed by the authors concerning the flux of iron from the surface, regeneration and constant deep water values could be incorporated easily into this framework. For a steady-state element such as iron, this model's equation for subsurface waters is:

$$0 = \frac{C_0(z) - C(z)}{\tau} - k_1 C(z) + k_2 R(z)$$

where $C_0(z)$ = the concentration of iron in the surface waters which ventilate water at the depth z, C(z) = the concentration of iron at a depth z, τ = the ventilation residence time of water at depth z, k_1 = the scavenging rate constant, k_2 = the stoichiometric ratio of iron released compared to oxygen consumed ($\Delta Fe/-\Delta O_2$) and R(z) = the oxygen utilization rate at depth z.

This model is no more complex than the diffusive-only model, but it is better because it is consistent with the temperature-salinity structure (as determined by the $C_0(z)$ for these properties) and it will give the right ventilation age so as to be consistent with the transient tracers. As stated, it does not include the 'magic' 0.6 for the deep waters, but this concept could be easily included ('if calculated value below 1 km is less than 0.6, set value to 0.6').

5. Summary

I regard the statement that 'The simple model that we have developed here explains nearly all of the variability that is seen in open ocean profiles' with a grain of sea salt. First, certain things simply are assumed (e.g. constant deep ocean Fe) and not really explained. Second, curve fitting is a marvelous thing to play with, but it shouldn't be taken seriously.

None of this criticism should be taken to detract in any way from the importance of the paper in its presentation of a picture of how iron is distributed in the ocean. The concepts of Johnson et al. concerning control of iron in the deep ocean via solubility or a chelator can be tested through further observations and need not be dismissed out of hand.

In a review of Imbrie and Imbrie's stirring tale of heroism in paleoclimate research ('Ice Ages: Solving the Mystery', Imbrie and Imbrie, 1979), Wally Broecker suggested that despite the many advances in knowledge chronicled by the Imbries, there was still much to learn before the mystery of the ice ages could be considered solved. In other words, there was room on the climatic stage for more heroes. I would suggest that Johnson et al. and others have heroically opened the door to the distribution and behavior of iron in the ocean, but there is still much to be done before we understand what controls dissolved iron concentrations in the world ocean. Johnson et al. have made remarkable success in illuminating the distribution of iron in the ocean. That achievement is not diminished by arguments that we don't yet really understand how that distribution is controlled.

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