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## Comment on "Molybdenum Isotope Evidence for Widespread Anoxia in Mid-Proterozoic Oceans"

Arnold *et al.* (1) reported Mo isotope compositions of mid-Proterozoic black shale, which were different from those of euxinic sediments in the Black Sea. On the basis of a mass balance model calculation, they claimed that "the area of oxic sedimentation in the mid-Proterozoic oceans was nearly a factor of 10 smaller than the modern value, or the area of euxinic sedimentation approached a factor of 10 larger than the modern value, or, most likely, an intermediate situation occurred involving both substantial contraction of the extent of oxic deposition and expansion of the euxinic deep ocean." Thus, they suggested that a widespread anoxia occurred in mid-Proterozoic oceans. However, this conclusion seems based on misinterpretation of their model calculation results.

According to the Arnold *et al.* calculation of total Mo removal, the fraction of Mo removal to Mn-oxide ( $f_{ox}$ ) was ~30% and of Mo removal to euxinic sediment ( $f_{eux}$ ) was ~70% in the mid-Proterozoic. Today,  $f_{ox}$  is ~75% and  $f_{eux}$  is ~25%. Thus, the ratio ( $f_{ox}/f_{eux}$ ) changed from <0.4 in the mid-Proterozoic to 3 today. On the basis of this number, Arnold *et al.* (1) suggested widespread anoxia in mid-Proterozoic oceans. However, it is the ratio of the Mo fraction removed to oxic sediment to that removed to euxinic sediment ( $f_{ox}/f_{eux}$ ) that changed 10-fold, rather than the Mo fractions themselves or the oxic deposition area. In fact, according to Arnold *et al.* (1), the fraction of Mo removal to Mn-oxide changed from 30% in the mid-Proterozoic to 75% today, a change less than 3-fold. Our calculation using their model and data shows that oxic area in mid-Proterozoic oceans was predominant relative to euxinic area.

If we let  $F_{ox}$  and  $F_{eux}$  account for fluxes ( $\text{g m}^{-2} \text{ year}^{-1}$ ) of Mo to Mn-oxide and euxinic sediments, respectively, then the amount of Mo removal to Mn-oxide on an area of  $A_{ox}$  in a unit of time is  $A_{ox} \cdot F_{ox}$ , and the amount of Mo removal to euxinic sediment on an area of  $A_{eux}$  in a unit of time is  $A_{eux} \cdot F_{eux}$ . Assuming that the fractionation of Mo isotopes between seawater ( $\delta^{97/95}\text{Mo}_{sw}$ ) and Mn-oxide is spatially and temporally constant ( $\Delta_{sw-eux} = 2.1$ ) (1–3) and that Mo fractionation between seawater and euxinic sediment is small ( $\Delta_{sw-eux} = 0.3$  to 0; 0.3 is used in the following calculation) as a

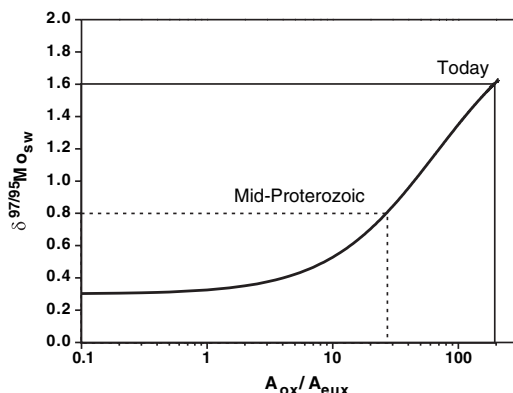
result of quantitative Mo removal at euxinic conditions (1, 4)—the input of Mo to oceans having an average  $\delta^{97/95}\text{Mo}$  value of zero (1, 2, 4) and a steady-state balance of Mo input and output and isotope composition (1, 4)—then Eq. 1 of Arnold *et al.* (1) can be written as

$$A_{eux} \cdot F_{eux} \cdot (\delta^{97/95}\text{Mo}_{sw} - \Delta_{sw-eux}) + A_{ox} \cdot F_{ox} \cdot (\delta^{97/95}\text{Mo}_{sw} - \Delta_{sw-ox}) = 0 \quad (1)$$

If we let  $F_{ox}/F_{eux} = K_{ox/eux}$ , which is a measure of relative Mo removal efficiency of oxic to euxinic sediments, similar to  $k_{ox}/k_{eux}$  of Arnold *et al.* [note 39 in (1)], then Eq. 1 becomes:

$$\delta^{97/95}\text{Mo}_{sw} = (\Delta_{sw-eux} + K_{ox/eux} \cdot \Delta_{sw-ox} \cdot A_{ox}/A_{eux}) / (1 + K_{ox/eux} \cdot A_{ox}/A_{eux}) \quad (2)$$

Eq. 2 relates seawater  $\delta^{97/95}\text{Mo}_{sw}$  value to the ratio of oxic area to euxinic area ( $A_{ox}/A_{eux}$ ). In modern oceans,  $K_{ox/eux} \leq (75\%/99.5\%)/ (25\%/0.5\%) \approx 0.015$ , because Mo removal to the euxinic seafloor (which covers <0.5% of the total modern seafloor) accounts for ~25% of annual Mo removal in the oceans, whereas Mo removal to oxic seafloor (which covers >99% of the total modern seafloor) accounts for ~75% of annual Mo removal (1, 2, 5–7). The  $K_{ox/eux}$  value is assumed to be constant [see note 39 in (1)]. Figure 1 shows the relation between  $\delta^{97/95}\text{Mo}_{sw}$  and the  $A_{ox}/A_{eux}$  ratio expressed by Eq. 2 using these parameters. It shows that the



**Fig. 1.** Model calculation result showing that the seawater  $\delta^{97/95}\text{Mo}_{sw}$  value varies as a function of  $A_{ox}/A_{eux}$  (ratio of oxic area to euxinic area). It shows that present-day  $A_{ox}/A_{eux} = \sim 200$  corresponds to  $\delta^{97/95}\text{Mo}_{sw} = 1.6\text{‰}$  and that mid-Proterozoic  $\delta^{97/95}\text{Mo}_{sw} = 0.8\text{‰}$  corresponds to  $A_{ox}/A_{eux} = \sim 27$ .

present-day  $A_{ox}/A_{eux}$  ratio is  $\sim 200$ , corresponding to seawater  $\delta^{97/95}\text{Mo}_{sw} = 1.6\text{‰}$ , whereas the mid-Proterozoic  $\delta^{97/95}\text{Mo}_{sw}$  of  $0.8\text{‰}$  corresponded to  $A_{ox}/A_{eux} = \sim 27$ . This means that in the mid-Proterozoic, the euxinic deposition area was only about 3.7% of the oxic deposition area. This oceanic state is not consistent with the claim of widespread anoxia, although the effect of suboxic area on oceanic Mo isotopes needs more constraints. This may also imply that only a few percent euxinic area in the oceans (e.g., the existence of several semiclosed sea basins similar to the present-day Black Sea) could produce  $\delta^{97/95}\text{Mo}$  values similar to those of the mid-Proterozoic black shale analyzed by Arnold *et al.* (1).

According to this model, when  $A_{ox}/A_{eux} < 10$ , the variation of  $\delta^{97/95}\text{Mo}_{sw}$  with  $A_{ox}/A_{eux}$  would be within analytical error ( $\sim 0.24\text{‰}$ ) (1), and thus  $A_{ox}/A_{eux}$  change cannot be resolved by the Mo isotopic method (Fig. 1). If at some point in geological history there were a state of widespread anoxia with euxinic area exceeding, say, 30%, then concentration and residence time of dissolved Mo in the ocean would decrease greatly. The  $\delta^{97/95}\text{Mo}$  value of euxinic sedimentary Mo would be close to that of input, and the oceanic Mo isotope fractionation would not be controlled by oxic sedimentation processes as today. Transition from such an anoxic condition to the oxic condition of today cannot be described using a steady-state model, as proposed by Arnold *et al.* (1).

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### References and Notes

- G. L. Arnold, A. D. Anbar, J. Barling, T. W. Lyons, *Science* **304**, 87 (2004).
- C. Siebert, T. F. Nagler, F. von Blanckenburg, J. D. Kramers, *Earth Planet. Sci. Lett.* **211**, 159 (2003).
- J. Barling, A. D. Anbar, *Earth Planet. Sci. Lett.* **217**, 315 (2004).
- J. Barling, G. L. Arnold, A. D. Anbar, *Earth Planet. Sci. Lett.* **193**, 447 (2001).
- S. R. Emerson, S. S. Huested, *Mar. Chem.* **34**, 177 (1991).
- J. L. Morford, S. Emerson, *Geochim. Cosmochim. Acta* **63**, 1735 (1999).
- K. K. Bertine, K. K. Turekian, *Geochim. Cosmochim. Acta* **37**, 1415 (1973).
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