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Response to Comment on “Molybdenum Isotope Evidence for Widespread Anoxia in Mid-Proterozoic Oceans”

Relating changes in Mo isotope signatures preserved in the geologic record to changes in the extent of seafloor anoxia is not a trivial exercise. We previously presented and interpreted new Mo isotope data as indicating expanded anoxia in mid-Proterozoic oceans, potentially reaching global extent (1). Ling *et al.* (2) challenge our conclusions, arguing that the data are not consistent with widespread anoxia. We stand by our original interpretation but welcome the opportunity to clarify and expand on those conclusions, particularly in view of the potential importance of ocean redox change for biological evolution (3).

It is important to emphasize that Ling *et al.* accept our data and largely recapitulate our calculations to arrive at the same first-order conclusion: Within the framework of a simple two-sink model, assuming linear scaling between the fraction of Mo removed to each sink and its areal extent, the data indicate that the ratio of oxic area to euxinic area (A_{ox}/A_{eux}) was smaller by a factor of 5 to 10 during the mid-Proterozoic than today ($A_{ox}/A_{eux} \sim 27$ versus 200 today, according to Ling *et al.*). Given our present understanding of Mo isotope systematics and the available data, there is no dispute that the mid-Proterozoic Mo isotope budget was perturbed as compared with today and that this perturbation is most easily explained in terms of less oxygenated oceans at that time. The dispute is over the quantitative oceanographic implications of this shift in A_{ox}/A_{eux} .

Ling *et al.* (2) interpret this result to mean that because mid-Proterozoic euxinic deposition area was only about 3.7% of oxic deposition area, the claim of widespread anoxia is not valid. We reject this interpretation because the 3.7% figure describes the relative sizes of the two sinks, not the absolute size of either (although not explicitly stated by Ling *et al.*, we assume that the figure was obtained as follows: $1/(A_{ox}/A_{eux}) \times 100\% = 1/27 \times 100\% = 3.7\%$). Therefore, this figure cannot uniquely constrain the areas of oxic or euxinic seafloor without an additional constraint (see below). This problem can be simply illustrated by comparison with the modern condition, $1/(A_{ox}/A_{eux}) \sim 1/200 \times 100\% = 0.5\%$ (2). The evolution of the oceans from a value of 3.7% in the mid-Proterozoic to 0.5% today

(a roughly 7-fold change) could have occurred in one of three ways. At one extreme, A_{eux} may have contracted by a factor of ~ 7 since the mid-Proterozoic. Indeed, this scenario would not imply widespread anoxia in the Proterozoic; seven times the modern euxinic area would still be a trivial fraction of the total seafloor. However, at the other extreme, A_{ox} may have expanded by a factor of ~ 7 . This scenario implies mid-Proterozoic oceans in which oxic sedimentation was vastly less common than today, fully consistent with a scenario of widespread oxygen deficiency. As stated in (1), it seems most likely that ocean evolution was characterized by a combination of substantial oxic contraction and euxinic expansion.

It is intuitively tempting to resolve this problem by adopting the constraint $A_{eux} + A_{ox} = \text{constant}$. This assumption dictates that a change in the area of A_{ox} must be balanced by an equal and opposite change in the area of A_{eux} , and vice versa. Quantitatively, it demands that nearly all the change in A_{ox}/A_{eux} was the result of a 7-fold change in the size of the euxinic sink; A_{ox} changes by only 4%. We suspect that Ling *et al.* (2) have this constraint in mind. However, this constraint is fundamentally unrealistic because it ignores the existence of areas of seafloor other than Mn-oxide-bearing sediments and sediments underlying euxinic waters [see note 40 in (1)]. Such areas include suboxic settings (where bottom water $O_2 < 5 \mu\text{M}$ but $H_2S \sim 0 \mu\text{M}$), settings that are anoxic but not euxinic (where $O_2 \sim H_2S \sim 0 \mu\text{M}$), and regions of carbonate sedimentation, detrital sediments, and the like. The existence of such areas permits A_{ox} and A_{eux} to vary independently. For example, A_{ox} could decrease independently of an increase in A_{eux} if there were an expansion of suboxic seafloor at the expense of oxic seafloor.

As discussed in (1), the situation deviates even further from the simple two-sink model of Ling *et al.*, because evidence suggests that sediments accumulating under suboxic bottom waters are also a small but important sink for Mo; estimates suggest that this sink could account for as much as 20% of Mo cycling today (4). For reasons not fully understood, this sink fractionates Mo isotopes in the same direction as the oxic sink, that is, Mo isotopes in suboxic

sediments are lighter than in seawater, as is the case with oxic sediments (5). Additionally, porewater studies in suboxic settings indicate that the net magnitude of fractionation during removal of Mo from seawater to suboxic sediments may be similar to fractionation by the oxic sink (6–8). As a result, in contrast to increases in A_{eux} , increases in the area of suboxic seafloor at the expense of A_{ox} have little or no impact on the Mo isotope system. It is difficult to imagine real ocean basins in which A_{eux} increases and A_{ox} decreases substantially without a substantial increase in A_{sub} . Therefore, we concluded that mid-Proterozoic f_{ox}/f_{eux} was less than 0.4 rather than equal to 0.4 (1), a finding that would translate here into $A_{ox}/A_{eux} < 27$, not $A_{ox}/A_{eux} = 27$. In fact, the Mo isotope data are consistent with mid-Proterozoic oceans in which A_{ox}/A_{eux} approached 0 and most of the seafloor was overlain by waters with $0 \mu\text{M} < O_2 < 5 \mu\text{M}$.

Although the efficiency with which Mo is removed to suboxic sediments is poorly known, it appears to be intermediate between the removal efficiencies in oxic and euxinic settings. Hence, it is likely that such oceans would have been typified by depressed Mo concentrations relative to today's, but not so depressed as to eliminate all authigenic enrichment of Mo. The moderate Mo enrichments in mid-Proterozoic black shales, implying ocean Mo concentrations that were depressed but within an order of magnitude of today's (1), fit this scenario.

Ling *et al.* conclude their comment by questioning our use of a steady-state model to describe the transition between anoxic and oxic conditions. We do not understand this critique because we apply this model to the apparently long-lived steady state between the major redox transitions of the Paleoproterozoic and Neoproterozoic. Such application of steady-state box models is not unusual.

Further study of the Mo elemental and isotope budgets will improve our ability to draw quantitative conclusions about changes in ocean anoxia from measured Mo isotope signatures. In the meantime, the possibility of widespread oxygen deficiency in mid-Proterozoic oceans, and its consequences for evolution, cannot be discounted.

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