

TECHNICAL COMMENT

Technical comment on “Reexamination of 2.5-Ga ‘whiff’ of oxygen interval points to anoxic ocean before GOE”

Ariel D. Anbar^{1,2*}, Roger Buick³, Gwyneth W. Gordon¹, Aleisha C. Johnson⁴, Brian Kendall⁵, Timothy W. Lyons⁶, Chadlin M. Ostrander⁷, Noah J. Planavsky⁸, Christopher T. Reinhard⁹, Eva E. Stüeken¹⁰

Many lines of inorganic geochemical evidence suggest transient “whiffs” of environmental oxygenation before the Great Oxidation Event (GOE). Slotznick *et al.* assert that analyses of paleoredox proxies in the Mount McRae Shale, Western Australia, were misinterpreted and hence that environmental O₂ levels were persistently negligible before the GOE. We find these arguments logically flawed and factually incomplete.

Slotznick *et al.* (1) hypothesize that molybdenum (Mo) and rhenium (Re) were introduced to the Mount McRae Shale as constituents of volcanogenic glasses or (in the case of Re) as volcanogenic volatiles, which subsequently altered to form secondary sulfide minerals. These processes are invoked to explain previously observed enrichments of Mo and Re and shifts in the stable isotope composition of Mo ($\delta^{98}\text{Mo}$). This “volcanogenic hypothesis” contrasts with the “whiff hypothesis,” built on extensive prior published research into the incorporation and preservation of Mo and other redox-sensitive elements in sedimentary rocks. According to the whiff hypothesis, enrichments of Mo and Re and shifts in $\delta^{98}\text{Mo}$ reflect changes in the ocean budgets of Mo and Re, which, in turn, were affected by oxidative weathering and transport (2, 3). Extensive independent data corroborate the whiff hypothesis [reviewed in (4)].

Slotznick *et al.* (1) focus on the petrogenesis of sulfide minerals in the “whiff” interval of the Mount McRae Shale, documenting various postdepositional processes. We do not dispute that these 2.5-billion-year (Ga)-old sedimentary rocks host secondary sulfide minerals with a complex history. It would be unexpected if this was not the case. For this reason, prior studies avoided sampling macroscopic sulfide nodules and veins, instead focusing on the fine-grained carbonaceous matrix that constitutes the vast majority of these black shales. Pyrite laminae were in some instances unavoidable [see, e.g., supplementary materials of (2)] but likely formed early. Bulk-rock chemical analyses can be used to evaluate the influence of laminae and finely disseminated pyrite on elemental and isotopic distributions.

¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ, USA.

²School of Molecular Sciences, Arizona State University, Tempe, AZ, USA.

³Department of Earth and Space Sciences, University of Washington, Seattle, WA, USA.

⁴Department of Geosciences, University of Arizona, Tucson, AZ, USA.

⁵Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, Canada.

⁶Department of Earth and Planetary Sciences, University of California Riverside, Riverside, CA, USA.

⁷Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Falmouth, MA, USA.

⁸Department of Earth and Planetary Sciences, Yale University, New Haven, CT, USA.

⁹Department of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA.

¹⁰School of Earth and Environmental Sciences, University of St. Andrews, Scotland, UK.

*Corresponding author. Email: anbar@asu.edu

Copyright © 2023 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

In focusing on secondary sulfides, Slotznick *et al.* (1) overlook data more directly related to primary depositional conditions. In the fine-grained matrix, Mo and Re concentrations are well correlated (Fig. 1), but neither correlate well with pyrite sulfur (Fig. 2A). These observations are inconsistent with arguments that Mo and Re are hosted in different phases and that the Mo enrichment in the whiff interval was created by postdepositional sulfide mineralization (1). Instead, Mo and Re are both primarily associated with organic matter (Fig. 2B), indicating a common nonsulfide carrier phase. A precise age of $\sim 2.495 \pm 0.014$ Ga (2, 5) from a well-defined Re-Os isochron for these rocks is demonstrably depositional via agreement with U-Pb zircon ages in interbedded tuffs (1). If the Re-Os age is depositional, then it follows that the Re enrichment is a primary feature—and so, too, the highly correlated Mo enrichment.

Could the Mo enrichment be primary but derived from volcanogenic glass rather than seawater? While we do not dispute evidence of volcanogenic glass in these sedimentary rocks (1) nor important recent work showing that glass is a major host phase of Mo in basalts (6), we find it implausible that the measured whole-rock

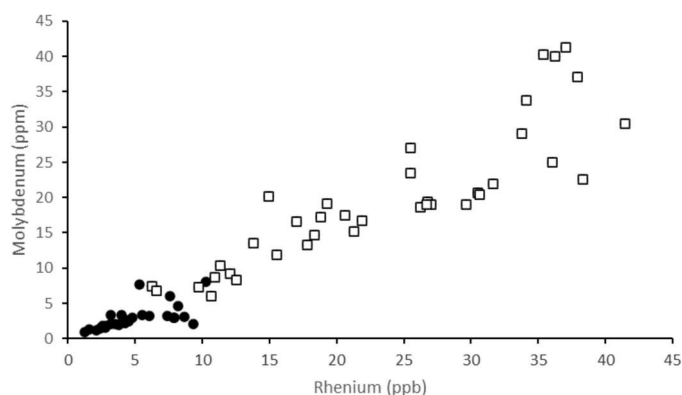


Fig. 1. Correlation of Re and Mo. A strong correlation between Re and Mo concentrations in the organic-rich, fine-grained matrix of the Mount McRae Shale points to a common host phase for these metals. Squares, 126- to 153-m whiff interval; circles, 158- to 189-m pre-whiff interval (drill core ABDP-9). Data from (2). ppb, parts per billion.

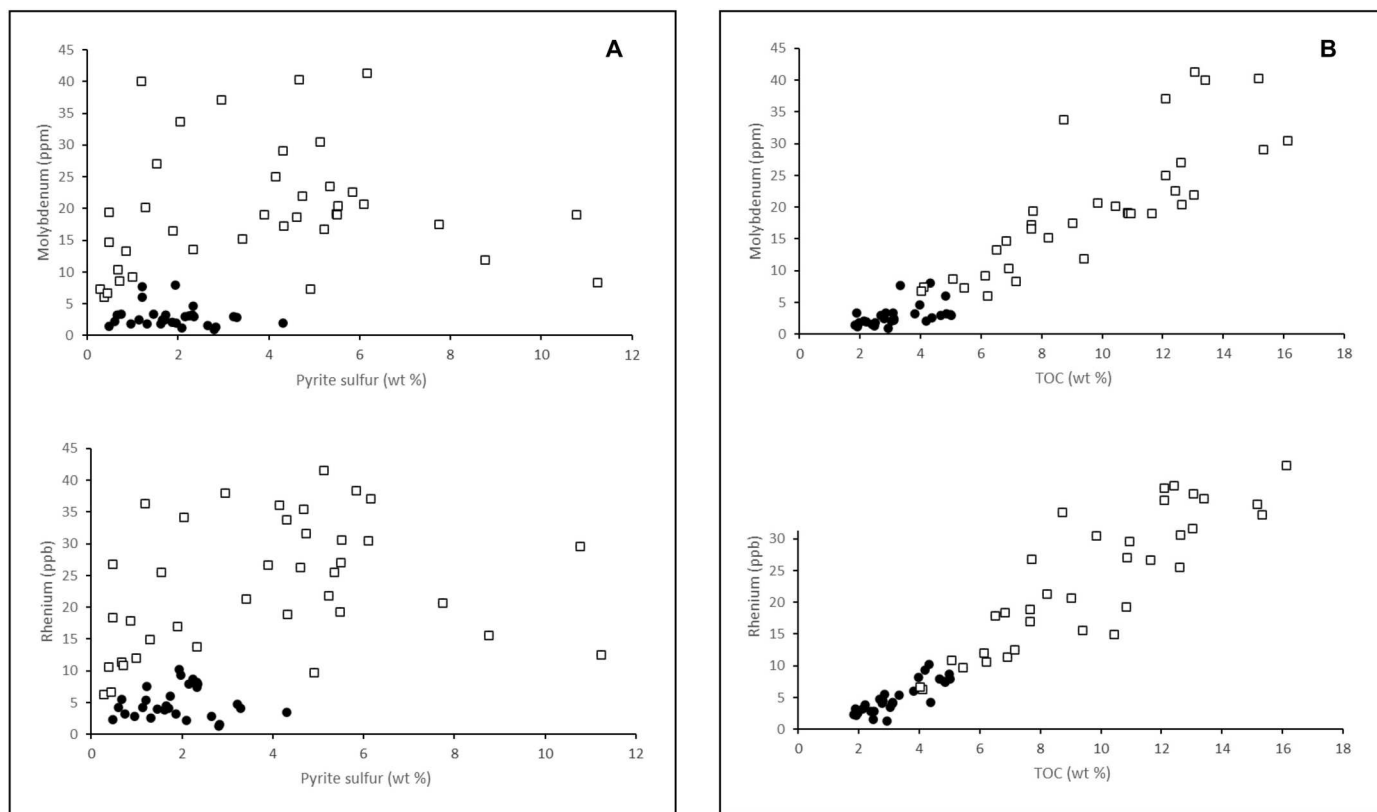


Fig. 2. Correlations of Re and Mo with TOC and pyrite sulfur. (A and B) Re and Mo concentrations are strongly correlated with total organic carbon (TOC) but not with pyrite sulfur, suggesting that these metals are primarily hosted by organic matter rather than sulfide minerals in the fine-grained organic-rich matrix of the Mount McRae Shale. Squares, 126- to 153-m whiff interval; circles, 158- to 189-m pre-whiff interval (drill core ABDP-9). Data from (2, 10). wt %, weight %.

enrichments of Mo of up to 40 parts per million (ppm) in these rocks arose from input of volcanogenic glasses containing Mo of order 10 ppm (6). This scenario requires massive removal of bulk material while preferentially retaining Mo. The material removal problem is compounded by $\delta^{98}\text{Mo}$ data, which show a shift heavyward relative to crustal inputs during the whiff interval, by up to $\sim 1.8\text{‰}$ (3). Slotznick *et al.* (1) propose that this shift is a consequence of preferential incorporation of isotopically heavy Mo in secondary pyrite minerals formed under hydrothermal conditions, a recently found process (7, 8). However, this explanation requires removal of isotopically light Mo to maintain isotope mass balance—all while the Re-Os system records no appreciable postdepositional disturbance, and the Mo-Re correlation shows no variation across the whiff interval. This scenario seems exceedingly unlikely. Slotznick *et al.* (1) do not consider these issues nor do they comment on the similarities between the geochemistry of these sedimentary rocks and that of much younger organic-rich shales lacking volcanogenic inputs or complex diagenetic histories. They also do not address why Mo and Re abundances in the Mount McRae Shale are low shortly before the whiff interval despite substantial volcanic input revealed by recent mercury isotope analyses (9).

The arguments in Slotznick *et al.* (1) are problematic in other ways. For example, they observe that the extreme organic carbon enrichment in the Mount McRae Shale requires a locally highly reducing environment, which they argue contradicts the whiff

hypothesis. However, the occurrence of highly reducing local environments is a well-understood, expected consequence of broader biospheric oxygenation (10). Weathering of igneous pyrites by trace levels of O_2 can deliver sulfate to the oceans where it can undergo microbial reduction to H_2S in locations of high primary production. Recognition that the Mount McRae Shale was deposited in such a local environment, based on independent evidence (10), is integral to all interpretations of these rocks (4).

Elsewhere, Slotznick *et al.* (1) cite nonzero sulfur mass-independent fraction (S-MIF) as evidence of persistent global anoxia. They neglect recent work showing that the O_2 levels needed to explain pre-Great Oxidation Event (GOE) Mo enrichments are compatible with nonzero S-MIF (11).

Last, Slotznick *et al.* (1) fail to offer alternative explanations for the many other inorganic tracers in the Mount McRae Shale that support the whiff hypothesis. These include correlated shifts in nitrogen, selenium, thallium, and uranium isotope ratios, each independently best explained by trace levels of O_2 [reviewed in (4)]. Collectively, these proxies, together with well-correlated Mo and Re enrichments, $\delta^{98}\text{Mo}$ variations, and the depositional Re-Os age, paint a coherent picture consistent with all other available data—including the detailed new observations contributed by Slotznick *et al.* (1). Furthermore, the whiff hypothesis is consistent with geochemical and paleontological studies of other Archean sedimentary sequences showing evidence of low levels of O_2 during at least some times, reviewed in (4), including from the

correlative ~2.5-Ga Klein Naute Formation (South Africa) and extending at least as far back as the ~3.23-Ga Manzimnyama Banded Iron Formation (South Africa). It is also consistent with recent phylogenetic studies indicating that O₂-producing photosynthesis evolved well before the GOE (12, 13).

Environmental interpretations derived from ancient rocks demand careful and constant scrutiny, so we welcome new data (1). However, when all available evidence is considered, it points to transient oxygenation before Earth's transition to an oxygenated world (4, 14).

REFERENCES AND NOTES

1. S. P. Slotznick, J. E. Johnson, B. Rasmussen, T. D. Raub, S. M. Webb, J.-W. Zi, J. L. Kirschvink, W. W. Fischer, Reexamination of 2.5-Ga "whiff" of oxygen interval points to anoxic ocean before GOE. *Sci. Adv.* **8**, eabj7190 (2022).
2. A. D. Anbar, Y. Duan, T. W. Lyons, G. L. Arnold, B. Kendall, R. A. Creaser, A. J. Kaufman, G. W. Gordon, C. Scott, J. Garvin, R. Buick, A whiff of oxygen before the great oxidation event? *Science* **317**, 1903–1906 (2007).
3. Y. Duan, A. D. Anbar, G. L. Arnold, T. W. Lyons, G. W. Gordon, B. Kendall, Molybdenum isotope evidence for mild environmental oxygenation before the Great Oxidation Event. *Geochim. Cosmochim. Acta* **74**, 6655–6668 (2010).
4. C. M. Ostrander, A. C. Johnson, A. D. Anbar, Earth's first redox revolution. *Annu. Rev. Earth Planet. Sci.* **49**, 337–366 (2021).
5. B. Kendall, R. A. Creaser, C. T. Reinhard, T. W. Lyons, A. D. Anbar, Transient episodes of mild environmental oxygenation and oxidative continental weathering during the late Archean. *Sci. Adv.* **1**, e1500777 (2015).
6. A. T. Greaney, R. L. Rudnick, R. T. Helz, R. M. Gaschnig, P. M. Piccoli, R. D. Ash, The behavior of chalcophile elements during magmatic differentiation as observed in Kilauea Iki lava lake, Hawaii. *Geochim. Cosmochim. Acta* **210**, 71–96 (2017).
7. A. K. Kaufmann, T. Pettke, M. Wille, Molybdenum isotope fractionation at upper-crustal magmatic-hydrothermal conditions. *Chem. Geol.* **578**, 120319 (2021).
8. D.-X. Kong, K. Cao, J.-F. Xu, J. Li, W. Li, Molybdenum isotope systematics of subduction-related magmas from the Zhongdian region: Assessing the mo fractionation behavior in magmatic-hydrothermal processes. *Ore Geol. Rev.* **133**, 104089 (2021).
9. J. Meixnerová, J. D. Blum, M. W. Johnson, E. E. Stüeken, M. A. Kipp, A. D. Anbar, R. Buick, Mercury abundance and isotopic composition indicate subaerial volcanism prior to the end-Archean "whiff" of oxygen. *Proc. Natl. Acad. Sci. U.S.A.* **118**, e2107511118 (2021).
10. C. T. Reinhard, R. Raiswell, C. Scott, A. D. Anbar, T. W. Lyons, A late Archean sulfidic sea stimulated by early oxidative weathering of the continents. *Science* **326**, 713–716 (2009).
11. A. C. Johnson, C. M. Ostrander, S. J. Romaniello, C. T. Reinhard, A. T. Greaney, T. W. Lyons, A. D. Anbar, Reconciling evidence of oxidative weathering and atmospheric anoxia on Archean Earth. *Sci. Adv.* **7**, eabj0108 (2021).
12. J. S. Boden, K. O. Konhauser, L. J. Robbins, P. Sánchez-Baracaldo, Timing the evolution of antioxidant enzymes in cyanobacteria. *Nat. Commun.* **12**, 4742 (2021).
13. G. P. Fournier, K. R. Moore, L. T. Rangel, J. G. Payette, L. Momper, T. Bosak, The Archean origin of oxygenic photosynthesis and extant cyanobacterial lineages. *Proc. R. Soc. B* **288**, 20210675 (2021).
14. T. W. Lyons, C. T. Reinhard, N. J. Planavsky, The rise of oxygen in Earth's early ocean and atmosphere. *Nature* **506**, 307–315 (2014).

Acknowledgments: We thank B. Schoene for editorial handling and three anonymous reviewers for helpful feedback. **Funding:** We thank the NASA Astrobiology Program and Canada Research Chairs Program for supporting work on this comment. **Author contributions:** A.D.A. wrote the original comment with input from R.B., B.K., T.W.L., C.M.O., and E.V.S. and feedback from the other coauthors. Following review, the comment was revised by A.D.A., B.K., and C.M.O. with feedback from the other coauthors. Figures were prepared by B.K. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All underlying data are available in the publications cited.

Submitted 5 April 2022
Accepted 3 March 2023
Published 7 April 2023
10.1126/sciadv.abq3736