Response to comment on "Reexamination of 2.5-Ga 'whiff' of oxygen interval points to anoxic ocean before GOE"

Sarah P. Slotznick[1]*, Jena E. Johnson[2], Birger Rasmussen[3,4], Timothy D. Raub[5,6], Samuel M. Webb[7], Jian-Wei Zi[4], Joseph L. Kirschvink[8,9], Woodward W. Fischer[8]

Sedimentological, textural, and microscale analyses of the Mount McRae Shale revealed a complex postdepositional history, previously unrecognized in bulk geochemical studies. We found that metal enrichments in the shale do not reside with depositional organic carbon, as previously proposed by Anbar *et al.*, but with late-stage pyrite, compromising claims for a "whiff" of oxygen ~50 million years before the Great Oxygenation Event.

The first step in understanding the history preserved in ancient rocks requires asking and answering some critical questions: How did the rock form? How did the minerals present get there? In other words, where and when did the information get stored?

Several geochemical analyses of Archean sedimentary rocks have uncovered small enrichments of redox-sensitive metals [molybdenum (Mo) and rhenium (Re)] in pyritic carbonaceous shale. Among the earliest and most cited studies is that by Anbar *et al.* (*1*) from the 2.5-Ga Mount McRae Shale intersected in drill core ABDP-9, Western Australia. The correlation between metal abundance and organic carbon content led those authors to interpret that contemporaneous seawater was enriched in these metals, supplied from oxidative weathering of pyrite on land.

One limitation of Anbar *et al.*'s work (*1*) and many other redox proxies applied to the ABDP-9 core is that measurements were carried out on bulk samples (5 cm by 3 cm by 1 cm), destroying textural information and mixing depositional (primary) and nondepositional (secondary) components. We collected high-spatial resolution microscopic and analytical data to probe the origins of these signals for O_2 and answer the critical questions posed above (*2*). Our work revealed many stages of overprinting [at least five that we could date with U-Pb (*3*)]. These rocks have an exceedingly complex petrology; our data unraveling this history provide a framework for more nuanced reading of the chronicles recorded within them.

The usefulness of this textural approach is exemplified by the conspicuous development of a calcium sulfate, probably gypsum, within the fissile "whiff" interval in ABDP-9. A naïve interpretation of these observations might invoke that strata accumulated below sulfate-rich seawater in the highly evaporitic environment required

[1]Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA. [2]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48103, USA. [3]School of Earth Sciences, The University of Western Australia, Perth, Western Australia 6009, Australia. [4]State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, Hubei 430074, China. [5]School of Earth and Environmental Sciences, University of St Andrews, St Andrews, Fife, Scotland, KY16 9AL, UK. [6]Geoheritage Research Institute, Arlington Heights, IL 60005, USA. [7]Stanford Synchrotron Radiation Lightsource, Stanford University, Menlo Park, CA 94025, USA. [8]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA. [9]Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo 152-8550, Japan.
*Corresponding author. Email: sslotz@dartmouth.edu

to precipitate such a soluble salt. However, our textural and chemical imaging data make clear that this is an incorrect interpretation because cross-cutting relationships show that the sulfate mineralization was related to oxidative weathering taking place in recent time (*2*).
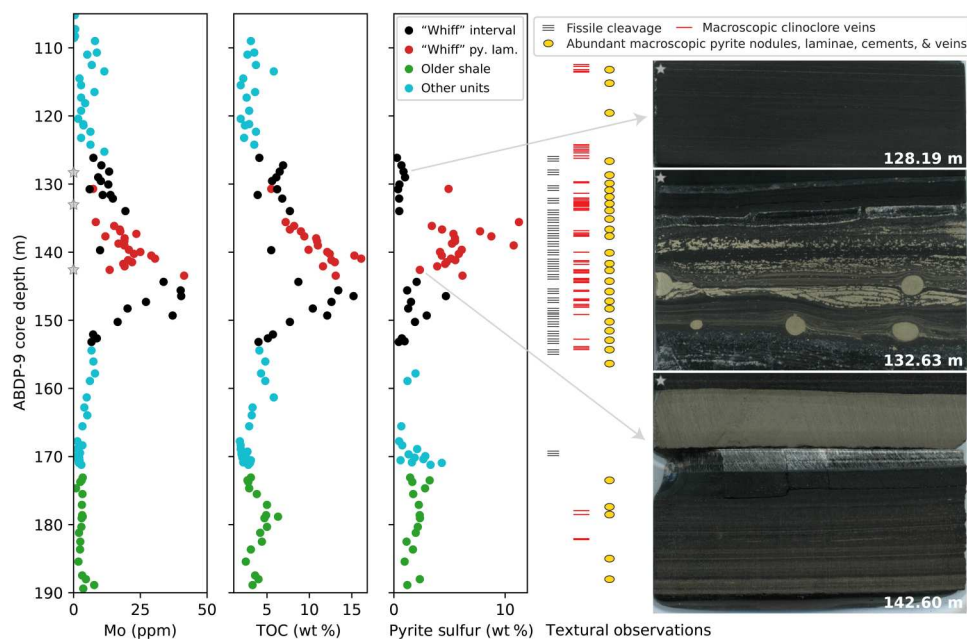
Anbar *et al.* (*4*) suggested that the Re and Mo enrichments are primary because a whole-rock rhenium-osmium (Re-Os) isochron yielded a plausible depositional age. Note the Re values in (*4*) used a different digestion (that dissolves silicates and some organics) than the Re-Os isochron's digestion (*5*) that targets organics (*6*). Re is enriched in volcanic glass (*7*), so it could have a similar source as Mo without affecting the Re-Os isochron. However, there are further problems with the interpretation of the Re-Os age, derived from samples collected across a 3.1-m interval. Our U-Pb zircon tuff ages (*2*) indicated that 3.1 m represents 3.2 to 5.5 million years. Because Os and Re residence times are 10,000 and 130,000 years, respectively (*8*, *9*), this violates the requirement that initial $^{187}Os/^{188}Os$ be identical between samples; the slope might reflect a mixing relationship rather than a true isochron [e.g., (*10*)].

Our study examined the petrogenesis of Mo; we observed that Mo is correlated with exceptionally high levels of arsenic (As) and hosted by late veins of cross-cutting pyrite and nodule-rims concentrated in highly fissile regions of the stratigraphy [figures 1, 2, and S11 of (*2*)]. Arsenic and other trace metals were also found in pyrite laminae [figures S8 and S9 of (*2*)], which were in 50% of the bulk whiff interval samples analyzed by Anbar *et al.* (*1*) (Fig. 1). Disseminated pyrite (*4*) is not simply early diagenetic [e.g., (*11*)]—our observations revealed disseminated pyrite mineralization focused along microfaults and cross-cutting mud particles [figure 1 of (*2*)]. There are many generations of pyrite apart from the one hosting Mo, so it is unsurprising that Mo and pyrite content do not correlate (*4*). Despite the hypotheses by Anbar *et al.* (*1*, *4*), we did not detect Mo in organic phases [figure S10 of (*2*)]. If the Mo entered the sediment via organic carbon (*1*, *4*), then it must have been mobilized during later metasomatic events to appear in the current host phases. Importantly, the organic content of the Mount McRae Shale is highest in the region where we observed the most fissile cleavage (Fig. 1). This is also where bulk Mo is highest, where secondary clinochlore veins are most abundant,

Fig. 1. Relationships between total organic carbon (TOC) and molybdenum (Mo) with permeable regions of abundant fissile cleavage and late mineralization (clinochlore veins and many generations of pyrite). Images with arrows come from within 2 cm of samples analyzed for bulk geochemistry. Pyrite laminae (py. lam.) demarcation from (*1*); pyrite sulfur calculated from (*13*). wt %, weight %.

and where secondary pyrite mineralization is maximal—a suite of observations that explain why organic carbon correlates with Mo.

We described several subequal hypotheses for the origin of the Mo, including a primary source in volcanic glass or a secondary introduction of Mo- and As-rich fluids (*2*). Anbar *et al.* (*4*) argue that enrichments from volcanic glass [Mo of ~10 parts per million (ppm)] cannot be enough to cause the observed amount in the whiff interval (up to 40 ppm). However, Mo in volcanic glass could have been intraformationally concentrated by late pyrite mineralization that preferentially targeted the whiff interval due to its fissile nature and inherent permeability (Fig. 1). If one integrates Mo across the entire column (and normalizes to 1 cm), then the calculated abundance is only 91 parts per billion (ppb) or, for just the whiff interval, 194 ppb. Thus, the Mo content of the entire volcaniclastic-rich Mount McRae Shale is unremarkable, and our observations showed that it was secondarily concentrated. Put simply, Mo is hosted by late mineralization and therefore cannot be used as a robust paleoenvironmental proxy.

All is not lost. Textural observations also pointed to signals that we can identify as primary—pyrite nodules with differential compaction [Fig. 1 and figures 1, S8, and S9 of (*2*)] with multiple sulfur isotopic signals that are only produced and preserved when global O_2 is <1 ppm (*2*, *12*). Furthermore, the unusually high organic carbon preservation at low sedimentation rates is a local signal indicating anoxic conditions in the Mount McRae Shale depositional environment. These two independent and primary observations from the original sediments point to anoxic oceans ~2.5 billion years ago.

REFERENCES AND NOTES

1. 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).

2. 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).

3. B. Rasmussen, J.-W. Zi, J. R. Muhling, D. J. Dunkley, W. W. Fischer, U-Pb dating of overpressure veins in late Archean shales reveals six episodes of Paleoproterozoic deformation and fluid flow in the Pilbara craton. *Geology* **48**, 961–965 (2020).

4. A. D. Anbar, R. Buick, G. W. Gordon, A. C. Johnson, B. Kendall, T. W. Lyons, C. M. Ostrander, N. J. Planavsky, C. T. Reinhard, E. E. Stüeken, Technical comment on "Reexamination of 2.5-Ga 'whiff' of oxygen interval points to anoxic ocean before GOE". *Sci. Adv.* , eadg1530 (2022).

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. D. Selby, R. A. Creaser, Re–Os geochronology of organic rich sediments: An evaluation of organic matter analysis methods. *Chem. Geol.* **200**, 225–240 (2003).

7. L. Pitcher, R. T. Helz, R. J. Walker, P. Piccoli, Fractionation of the platinum-group elements and Re during crystallization of basalt in Kilauea Iki Lava Lake, Hawaii. *Chem. Geol.* **260**, 196–210 (2009).

8. R. Oxburgh, Residence time of osmium in the oceans. *Geochem. Geophys. Geosyst.* **2**, 2000GC000104 (2001).

9. C. A. Miller, B. Peucker-Ehrenbrink, B. D. Walker, F. Marcantonio, Re-assessing the surface cycling of molybdenum and rhenium. *Geochim. Cosmochim. Acta* **75**, 7146–7179 (2011).

10. D. Y. Sumner, S. A. Bowring, U Pb geochronologic constraints on deposition of the Campbellrand Subgroup, Transvaal Supergroup, South Africa. *Precambrian Res.* **79**, 25–35 (1996).

11. W. W. Fischer, D. A. Fike, J. E. Johnson, T. D. Raub, Y. Guan, J. L. Kirschvink, J. M. Eiler, SQUID–SIMS is a useful approach to uncover primary signals in the Archean sulfur cycle. *Proc. Natl. Acad. Sci. U.S.A.* **111**, 5468–5473 (2014).

12. A. A. Pavlov, J. F. Kasting, Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* **2**, 27–41 (2002).

13. 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).