



## TECHNICAL RESPONSE

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

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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.

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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 non-depositional (secondary) components. We collected high-spatial resolution microscopic and analytical data to probe the origins of these signals for O<sub>2</sub> 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

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).

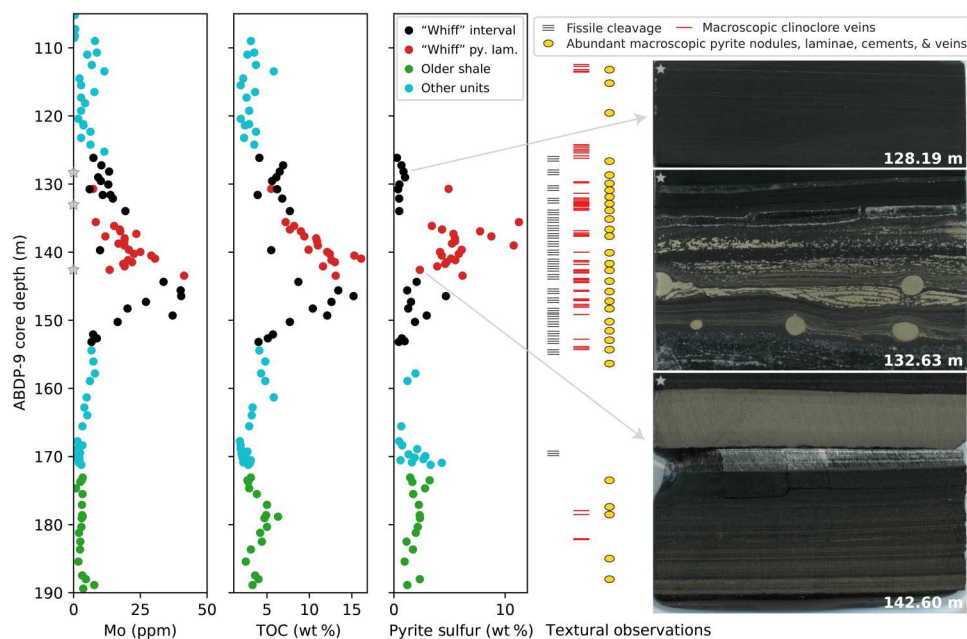
Anbar *et al.* (4) suggested that the Re and Mo enrichments are primary because a whole-rock rhenium-osmium (Re-Os) isochron yielded a plausible depositional age. Note the Re values in (4) used a different digestion (that dissolves silicates and some organics) than the Re-Os isochron's digestion (5) 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 <sup>187</sup>Os/<sup>188</sup>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 clinocllore veins are most abundant,

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**Fig. 1. Relationships between total organic carbon (TOC) and molybdenum (Mo) with permeable regions of abundant fissile cleavage and late mineralization (clinocllore 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 volcanoclastic-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.

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**Acknowledgments:** We thank B. Schoene for editorial management and feedback that helped improve this article. **Funding:** There are no funding sources for this response to the comment. See the work by Slotznick *et al.* (2) for funding of the original research. **Author contributions:** S.P.S., J.E.J., B.R., and W.W.F. wrote and revised the response incorporating comments from J.L.K. S.P.S. and J.E.J. drafted the figure incorporating images from T.D.R. All authors contributed to the initial publication through its conceptualization, data development, and/or analysis referenced throughout this response. **Competing interests:** The authors declare that they have

no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and in the original article (2).

Submitted 5 December 2022

Accepted 3 March 2023

Published 7 April 2023

10.1126/sciadv.adg1530