No evidence for high atmospheric oxygen levels 1,400 million years ago

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Zhang et al. (1) recently proposed atmospheric oxygen levels of ∼4% present atmospheric levels (PAL) based on modeling a paleoenvironment reconstructed from trace metal and biomarker data from the 1,400 Ma Xiamaling Formation in China. Intriguingly, this pO_2 level is above the threshold oxygen requirements of basal animals and clashes with evidence for atmospheric oxygen levels <<1% PAL in the mid-Proterozoic (2). However, there are fundamental problems with the inorganic and organic geochemical work presented by Zhang et al. (1).

The authors infer oxic deposition of the Xiamaling Formation based principally on the predominance of low V/Al ratios relative to a modern crustal average, which they attribute to V loss from the sediment (1). However, significant variability in detrital V/Al ratios of the upper crust make small local metal enrichment/deficiency patterns extremely difficult to identify. For example, in the upper portion of soil horizons in the continental United States, which will ultimately become detrital marine sediment, low (relative to the crustal average) V/Al ratios are found over large areas—the largest such area in the United States is >800,000 km^2 (Fig. 1), comparable to the catchment size of major rivers like the Brahmaputra and the Danube. Given the extent of detrital V variability and the possibility for temporal variability in detrital ratios within a section, the examined "oxic" intervals (1) in the Xiamaling could easily have V enrichments of several parts per million (similar to observed U and Mo enrichments). Further, there is no strong justification that riverine fluxes, in terms of elemental compositions, were constant over ∼400,000 years that encompassed the examined portion of the Xiamaling Formation. Lastly, numerous environmental factors, including rapid sedimentation rates, basin restriction, and global reservoir drawdown, can lead to low trace metal enrichments in anoxic marine settings (e.g., refs. 3 and 4). Consequently, the trace metal data presented by Zhang et al. (1) lack the resolving power to justify the conclusion of oxic bottom waters.

The paleoenvironmental reconstruction of Zhang et al. (1) also relies heavily on the presence of diagnostically euxinic biomarkers from the inferred overlying oxygen minimum zone (OMZ). However, the reported organic geochemistry does not meet recently established standards for Precambrian biomarker work (e.g., ref. 5). Reported 2,3.6-trimethyl aryl isoprenoids (2,3,6-TMAIs), likely sourced from anoxygenic phototrophic bacteria, were found in all samples and are most easily discerned in the chromatograms from a sample with 0.08 wt% TOC—the sample most easily contaminated by exogenous hydrocarbons. These compounds were not found in other recent biomarker work on the Xiamaling Formation (6), which used the cleaner, currently accepted methods. Similarly, the reports of steranes and methylsteranes by Zhang et al. (1) contradict recent findings in the Xiamaling and Proterozoic rocks more broadly (e.g., ref. 6). Both compound classes (2,3,6-TMAIs and steranes) are common contaminants in Precambrian sedimentary rocks (7). Because Zhang et al.'s study (1) does not follow the lead of recent organic research (e.g., refs. 5, 6, and 8), the data should be viewed with caution until they can be replicated using protocols now established within the Precambrian research community. Pending this confirmation, and given our reasonable concerns about their trace metal data, there remains no robust evidence for high atmospheric oxygen levels that could have fostered animal life 1,400 million years ago.

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Author contributions: N.J.P., D.B.C., C.T.R., C.D., G.D.L., G.L., K.O.K., and T.W.L. designed research; D.B.C. and S.Z. performed research; and N.J.P. and G.D.L. wrote the paper.

The authors declare no conflict of interest.

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 www.pnas.org/cgi/doi/10.1073/pnas.1601925113

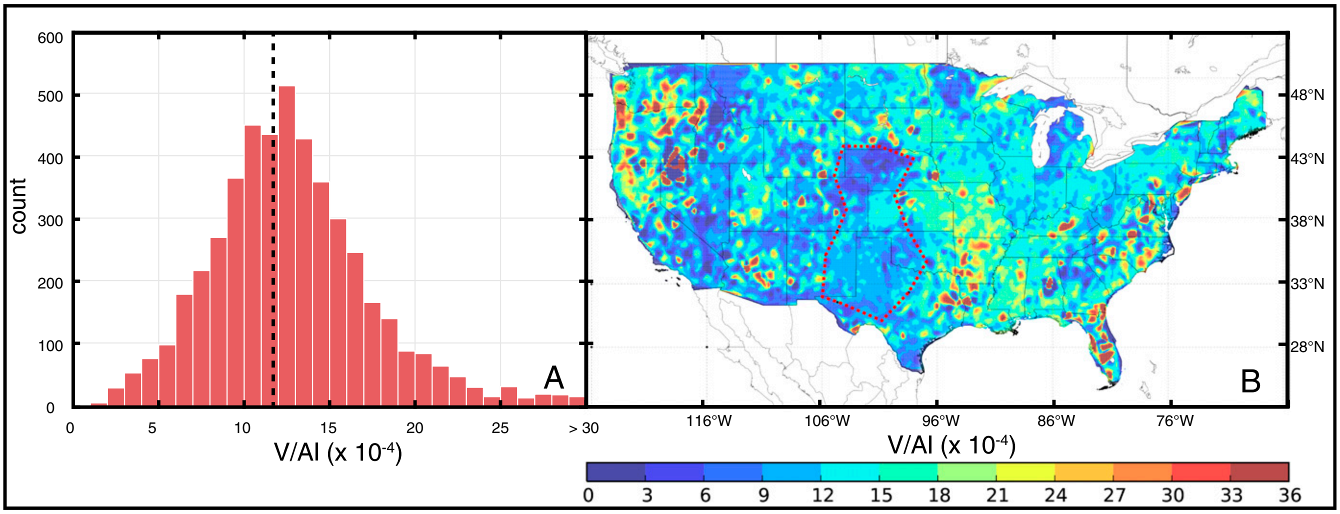

Fig. 1. **V/Al ratios of topsoils (0–5 cm depth) across the continental United States. (*A*) Variation in V/Al ratios from (9). The mean V/Al ratio is 13.28 ± 12.76 (2 SD), whereas the crustal average of Zhang et al. (1) (11.9) is shown by the dashed line. (*B*) V/Al ratios of topsoils across the United States. Dashed area represents an area of ~816,200 km^2 with a mean V/Al ratio of 10.1. Data are from ref. 9.**

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