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Evidence for benthic oxygen production in Neoarchean lacustrine stromatolites

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ABSTRACT

The evolution of oxygenic photosynthesis fundamentally altered the global environment, but the history of this metabolism prior to the Great Oxidation Event (GOE) at ca. 2.4 Ga remains unclear. Increasing evidence suggests that non-marine microbial mats served as localized "oxygen oases" for hundreds of millions of years before the GOE, though direct examination of redox proxies in Archean lacustrine microbial deposits remains relatively limited. We report spatially distinct patterns of positive and negative cerium (Ce) anomalies in lacustrine stromatolites from the 2.74 Ga Ventersdorp Supergroup (Hartbeesfontein Basin, South Africa), which indicate that dynamic redox conditions within ancient microbial communities were driven by oxygenic photosynthesis. Petrographic analyses and rare earth element signatures support a primary origin for Ce anomalies in stromatolite oxides. Oxides surrounding former bubbles entrained in mats (preserved as fenestrae) exhibit positive Ce anomalies, while oxides in stromatolite laminae typically contain strong negative Ce anomalies. The spatial patterns of Ce anomalies in Ventersdorp stromatolites are most parsimoniously explained by localized Ce oxidation and scavenging around oxygen bubbles produced by photosynthesis in microbial mats. Our new data from Ventersdorp stromatolites supports the presence of oxygenic photosynthesis ~300 m.y. before the GOE, and add to the growing evidence for early oxygen oases in Archean non-marine deposits.

INTRODUCTION

The release of free oxygen via oxygenic photosynthesis has shaped Earth's surface for billions of years, yet the onset and extent of early oxygen production remains uncertain. The youngest estimate for the origin of oxygenic photosynthesis is provided by the Great Oxidation Event (GOE) at ca. 2.4 Ga, when sedimentary and geochemical proxies indicate oxidizing surface environments (e.g., Farquhar, 2000; Holland, 2002). Two prevailing hypotheses exist regarding the relationship between early oxygen production and the GOE: (1) oxygenic photosynthesis evolved hundreds of millions of years before the GOE, but nutrient limitation, ecological competition, and redox buffering by abundant reducing compounds in Archean environments prevented oxygen accumulation in the atmosphere and oceans until ca. 2.4 Ga (Kump and Barley, 2007; Hao et al., 2020), or (2) oxygenic photosynthesis evolved at ca. 2.4 Ga, with high rates of microbial oxygen production overpowering global redox buffers to produce the GOE relatively rapidly (Fischer et al., 2016; Slotznick et al., 2022).

Models of early oxygenic photosynthesis have proposed the presence of "oxygen oases", areas where oxygen production locally overpowered redox buffers to produce transient oxidative events in the Archean rock record (Kasting, 1991; Olson et al., 2013; Riding et al., 2014). Non-marine microbial mats are frequently proposed as oxygen oases to reconcile Neoarchean evidence for oxidative continental weathering under a reducing atmosphere (Stüeken et al., 2012; Lalonde and Konhauser, 2015). Modern analogues for lacustrine oxygen oases occur in benthic microbial communities from Antarctic lakes, where cyanobacteria increase oxygen concentrations in mats without oxidizing the overlying water column (Sumner et al., 2015). Microbial mats preserved as stromatolites are more likely to record primary signatures for oxygenic photosynthesis than non-biogenic deposits, including oxygen bubbles in cyanobacterial cones preserved as rounded fenestrae at the tips of conical stromatolites (Bosak et al., 2009, 2010). Archean lacustrine stromatolites therefore provide clear targets to test for oxygen oases (Buick, 1992; Wilmeth et al., 2019).

The ca. 2.74 Ga Hartbeesfontein Basin (Rietgat Formation, Ventersdorp Supergroup) in South Africa (Fig. 1) is an isolated half-graben of the Ventersdorp continental rift; its lacustrine setting is further supported by frequent, meter-scale facies shifts and intercalation with subaerial volcanic deposits (Karpeta, 1989; Wilmeth et al., 2019). The basin contains extensive stromatolitic chert beds with exquisite microbial textures including abundant rounded fenestrae that are interpreted as former bubbles formed by microbial gas production (Figs. 1 and 2) (Wilmeth et al., 2019). Fenestrae occur throughout the stromatolites and are not localized at cone apices (Wilmeth et al., 2019); similar mat textures can form through various metabolisms producing oxygen, methane, or other gases (Hoehler et al., 2001; Mata et al., 2012). Therefore, while Hartbeesfontein fenestrae indicate microbial gas production, additional evidence is required to determine the specific gases. We

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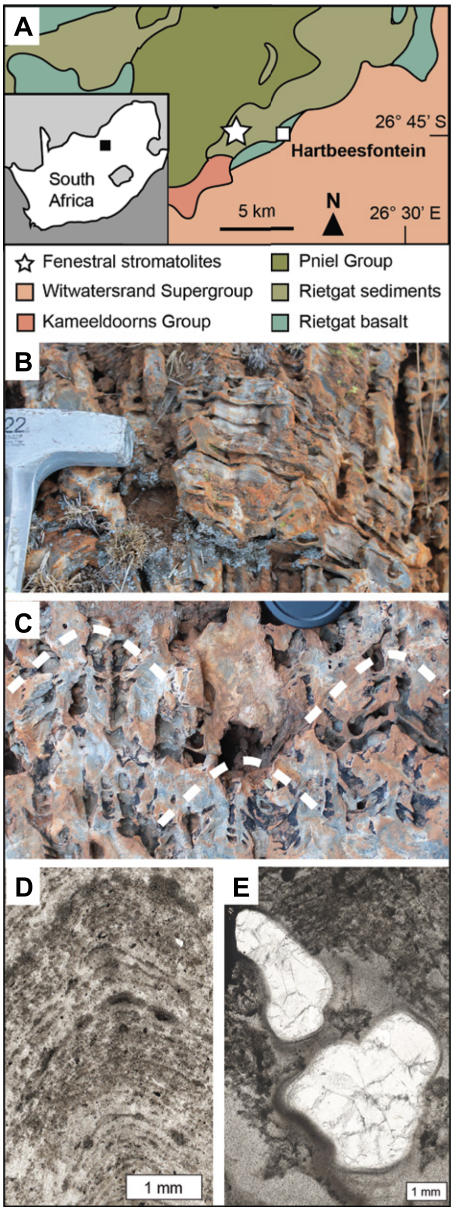

Figure 1. Hartbeesfontein Basin (South Africa) stromatolite textures. (A) Location map. Stromatolites are located at 26°46′7.86″S, 26°23′37.08″E. Black square in inset represents map location. (B,C) Domal stromatolitic chert; hammer head is 2 cm tall and lens cap is 6 cm. Dashed lines highlight the contours of stromatolite domes. (D) Conical stromatolite laminae. (E) Bubble fenestrae surrounded by microbial fabrics.

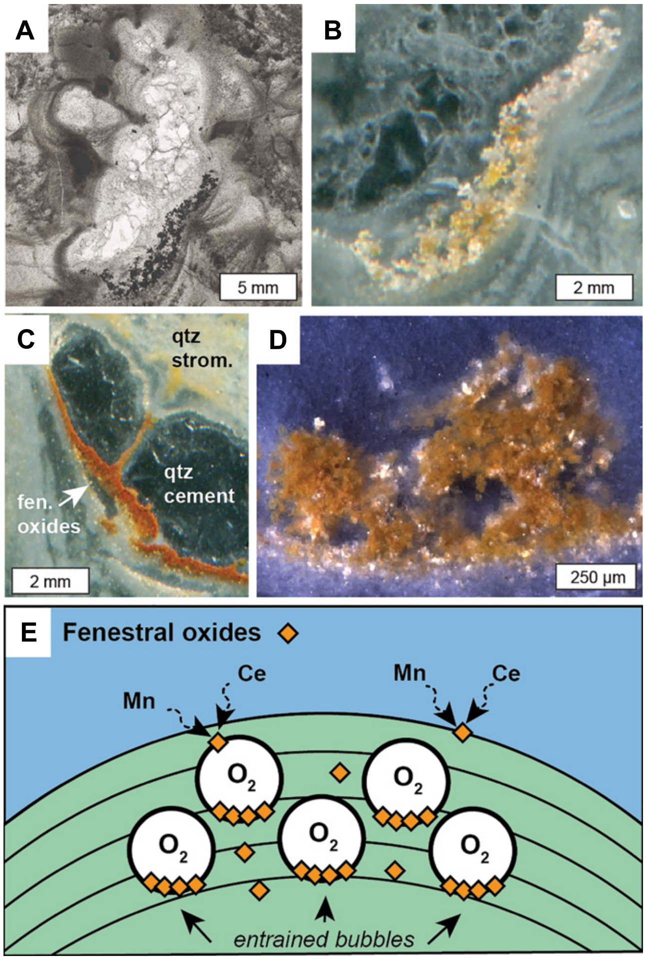

Figure 2. Fenestral oxides. (A,B) Bubble fenestra with extensive oxides along bottom margin viewed in plane-polarized and reflected light. (C,D) Fenestral (fen.) oxide viewed in reflected light. (E) Schematic of Mn and Ce oxidation and sorption onto fenestral oxides during mat growth. Qtz strom.—quartz stromatolite layers.

present new major and rare earth element (REE) data from Hartbeesfontein fenestral stromatolites to investigate the presence or absence of oxygenic photosynthesis in Archean lacustrine mats. We show distinct patterns of cerium (Ce) anomalies in fenestral and laminated stromatolite textures indicating localized oxygen production in microbial communities. Positive Ce anomalies around fenestrae are interpreted as oxidative Ce scavenging onto oxides around former bubbles, and negative anomalies in laminae indicate oxide precipitation where Ce has already been removed from oxidizing solutions.

RESULTS

REE Signatures of Oxides in Hartbeesfontein Stromatolites

Hartbeesfontein stromatolites contain three distinct oxide assemblages: in bubble fenestrae, stromatolite lamination, and weathering surfaces. Fenestral oxides appear orange and white in reflected light and reside at the contacts between fenestral walls and megaquartz, pore-filling cements, indicating early emplacement before cementation (Fig. 2; Fig. S3 in the Supplemental Material[1]; Wilmeth et al., 2019). Elemental composition of fenestral oxides measured by electron microprobe analyses (EMPA) revealed goethite, titanite, and a Mn-rich phase (Table S1). In contrast, oxides in stromatolite laminae are composed of isolated hematite crystals with associated goethite, as identified by Raman spectroscopy, EMPA, and reflected light microscopy (Fig. 3; Fig. S3; Table S1). Laminar oxides (10–30 μm in diameter) are visually distinct from fenestral oxides and exhibit metallic luster and variable black, red, and yellow coloration (Fig. 3). EMPA backscatter imaging revealed hexagonal and rhombohedral hematite crystal habits with partial dissolution features frequently containing goethite, supported by Raman spectra and light microscopy (Fig. 3; Fig. S3; Table S1). Recent surficial weathering surfaces also contain abundant red-orange iron oxides that cross-cut through primary fabrics (Fig. 3F).

Laser ablation–high-resolution–inductively coupled plasma–mass spectrometry (LA-HR-ICP-MS) of Hartbeesfontein stromatolites revealed distinct trace element signatures that differentiate fenestral, laminar, and surficial oxides (Fig. 4; Fig. S1). Recent weathering surfaces display flat REE signatures with mild negative Ce anomalies when normalized to post-Archean Australian shales (PAAS) and are an order of magnitude higher in total REE than crustal abundances (Fig. 4A). By contrast, laminar oxides deeper in stromatolite samples

[1]Supplemental Material. Supplementary discussion of geochemical and petrographic analyses, Table S1 (EMPA analyses of oxides in Hartbeesfontein stromatolites), and Table S2 (LA-ICP-MS analyses of oxides in Hartbeesfontein stromatolites). Please visit https://doi.org/10.1130/GEOL.S.19593439 to access the supplemental material, and contact editing@geosociety.org with any questions.

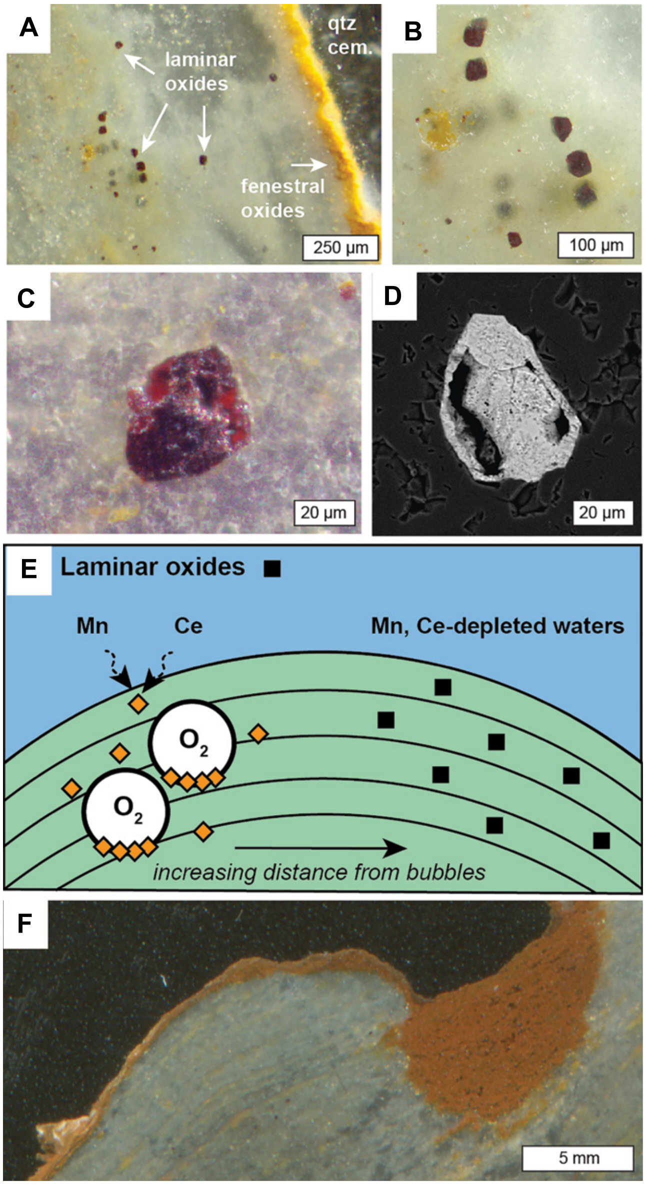

Figure 3. Laminar and surficial oxides. (A,B) Laminar oxides viewed under reflected light. Note the difference between laminar and fenestral oxides. (C) Laminar oxide with dissolution zones filled by orange goethite shown in reflected light. (D) Electron microprobe analysis (EMPA) back-scatter image of laminar oxide with dissolution zones. (E) Schematic of laminar versus fenestral oxides during mat growth. (F) Surficial oxides formed by recent weathering. Qtz cem.—quartz cement.

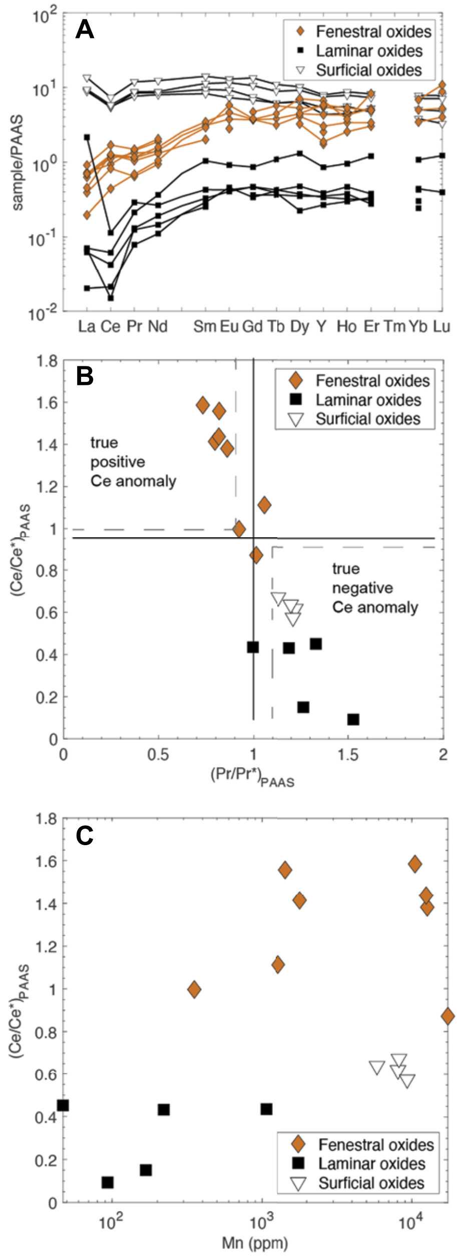

Figure 4. Rare earth element (REE) data from Hartbeesfontein Basin (South Africa) oxides. (A) REE + Y patterns in fenestral oxides, laminar, and surficial oxides. (B) Ce anomalies in different oxides. Areas inside dashed squares represent significant Ce anomalies. (C) Ce anomalies as a function of Mn concentration in oxides. PAAS—post-Archean Australian shales.

are REE-poor (~0.01–0.5 × crustal values) and show strong heavy REE (HREE)/light REE (LREE) enrichments (Fig. 4A). Fenestral oxides show intermediate total REE concentrations (~0.5–5 × crustal values) and lesser degrees of HREE enrichment.

Remarkably, laminar oxides frequently exhibit strong negative Ce anomalies, as low as 0.2 Ce/Ce*, with corresponding Pr/Pr* as high as 1.74 (Fig. 4B; calculations as per Bau and Dulski, 1996). Ce/Ce*, calculated on a log-linear scale according to Lawrence and Kamber (2006), reaches 0.21. In contrast, fenestral oxides contain significant positive Ce anomalies that reach 1.56 Ce/Ce* (Pr/Pr* as low as 0.70), corresponding to 2.02 Ce/Ce* on the same log-linear scale. One ICP-MS laser shot yielded an incomplete REE data set from which Ce anomalies could not be evaluated, and three anomalous laser shots contained significantly elevated LREE and Pb concentrations, which are not included in the figures but are noted in Table S2 and discussed in the Supplemental Material.

DISCUSSION

Primary Versus Secondary REE Signals

Previous petrographic analyses of Hartbeesfontein stromatolites (Wilmeth et al., 2019), such as paragenetic sequences of fenestral cements, indicate that fenestral and laminar oxides are *in situ*, derived from precursor minerals precipitated in Archean microbial mats . However, subsequent greenschist-grade metamorphism (Crow and Condie, 1988) and surficial weathering must be addressed before considering the environmental interpretations of REE signatures in oxide minerals. For example, hematite in Hartbeesfontein stromatolites is interpreted as the metamorphic product of metastable iron oxide precursors such as ferrihydrite, and goethite in laminar oxides is interpreted as secondary oxy-hydroxide precipitation in partially dissolved hematite crystals during surficial weathering.

REE patterns provide a powerful metric for distinguishing chemical signatures inherited during primary iron mineral precipitation (as indicated by petrography) versus secondary alteration (as indicated by mineralogy), as REEs are relatively immobile under most post-depositional conditions. Cerium anomalies are particularly attractive as a redox proxy, as oxidation from Ce(III) to Ce(IV) renders Ce more immobile relative to its neighbors, leading to its enhanced removal onto reactive particles such as Fe- and Mn-hydroxides (Byrne and Sholkovitz, 1996). The removal of Ce in oxidizing solutions produces negative Ce anomalies in associated chemical sediments, while Ce-scavenging particles themselves will contain positive Ce anomalies (Sholkovitz et al., 1994).

Alteration can produce secondary Ce anomalies after deposition (Hayashi et al., 2004; Bonnand et al., 2020; Planavsky et al., 2020). For example, exposed rock is more likely to contain Ce anomalies than less-weathered drill core (Planavsky et al., 2020), and Ce anomalies generated by Cenozoic alteration have been demonstrated in Paleoarchean rocks (Hayashi et al., 2004; Bonnand et al., 2020). Post-depositional negative Ce anomalies are best explained by secondary LREE enrichment from Ce-depleted aqueous solutions (Hayashi et al., 2004; Bonnand et al., 2020). Laminar and fenestral oxides have low LREE/HREE ratios (~0.1–0.01), which argues against significant post-depositional REE mobility. In contrast, secondary weathering surfaces on Hartbeesfontein stromatolites have negative Ce anomalies but are clearly differentiated from laminar and fenestral oxides by elevated REE concentrations (~10× crustal values) and high LREE/HREE ratios (Fig. 4A; Table S2). Therefore, while the current mineralogy of iron oxides in Hartbeesfontein stromatolites indicates a certain degree of secondary alteration, REEs in specific stromatolite textures (laminae and fenestrae) appear to maintain primary signatures of Archean lake chemistry.

Redox Conditions in Archean Lakes

The REE signatures of fenestral and laminar oxides in Hartbeesfontein stromatolites support previous interpretations of a lacustrine depositional environment (Karpeta, 1989). Marine Archean deposits typically contain yttrium/holmium ratios of >45 g/g (Kamber et al., 2004; Bolhar and van Kranendonk, 2007), and positive Eu anomalies indicate elevated hydrothermal input (Derry and Jacobsen, 1990). Both features are absent in Hartbeesfontein REE data (Fig. 4A) and other non-marine Archean deposits such as the Fortescue Group in Australia (Bolhar and van Kranendonk, 2007). Unlike Fortescue Group carbonates, Hartbeesfontein oxides are relatively depleted in LREE (~0.01–0.1× crustal values; Fig. 4A). While LREE depletion is more frequently observed in marine than non-marine deposits, lakes can exhibit a wide variety of LREE/HREE ratios, such as LREE-depleted waters with negative Ce anomalies in Lake Tanganyika, Africa (Barrat et al., 2000).

Positive Ce anomalies in Hartbeesfontein fenestral oxides indicate Ce sorption onto mineral surfaces under oxidizing conditions (Byrne and Sholkovitz, 1996). Oxidative Ce scavenging is especially prevalent on Mn- and Fe-Mn oxide surfaces (Byrne and Sholkovitz, 1996; De Carlo et al., 1997), and positive Ce anomalies in fenestral oxides are positively correlated with Mn concentration in Hartbeesfontein stromatolites (Fig. 4C). Conversely, negative Ce anomalies in laminar oxides (Fig. 4) indicate mineral precipitation in lake waters where Ce and Mn had previously been scavenged. The presence of positive and negative Ce anomalies in different stromatolite fabrics has two potential explanations, both of which require the presence of oxygenic photosynthesis in Archean lakes.

The presence of positive and negative Ce anomalies in Hartbeesfontein stromatolites could represent Ce shuttling across a redoxcline in the surrounding water column. In modern environments, Fe-Mn oxides remove Ce from oxygen-rich surficial waters and sink to lower depths (German et al., 1991; Byrne and Sholkovitz, 1996). Oxide dissolution in reducing deeper zones releases Ce back into surrounding waters, and chemical precipitates in such Ce-enriched areas will exhibit positive Ce anomalies (Glasby et al., 1987). In such a scenario, Hartbeesfontein stromatolites record a dynamic lacustrine chemocline that shifted above and below benthic microbial mats over time, where Ce-depleted laminar oxides precipitated in oxidizing lake waters, while Ce-enriched fenestral oxides formed in reducing zones as chemoclines shifted above mats.

Alternatively, the specific distribution of positive Ce anomalies in Hartbeesfontein fenestrae is more parsimoniously explained by localized Mn oxidation around oxygen bubbles entrained in microbial mats (Figs. 2E and 3E). Mn and Ce sequestration in fenestral oxides would correspondingly deplete concentrations in the surrounding layers of stromatolites, producing negative Ce anomalies in laminar oxides farther away from fenestrae. In modern mats, oxygen bubbles form similar loci for oxide precipitation in cyanobacterial communities (Raudsepp, 2012; Wilmeth et al., 2019). In anaerobic experiments simulating Archean environments, Raudsepp (2012) noted a wide variability in Mn/Fe ratios from oxides that precipitated in the same microbial mat (between <1:1 to >5:1). Therefore, Mn and Ce concentrations in stromatolites can vary due to redox gradients in microbial mats and do not necessarily require a shifting redoxcline in lake waters.

In Hartbeesfontein stromatolites, distributions of positive Ce anomalies around bubble fenestrae, surrounded by mat textures containing negative Ce anomalies, support the interpretation of fenestrae as loci of intense oxygenic photosynthesis in lacustrine microbial mats. While oxygen produced by the subaqueous stromatolites in our study is unlikely to have affected the oxidation of nearby terrestrial surfaces (e.g., Sumner et al., 2015), evidence for oxygenic photosynthesis in Archean lakes supports the presence of microbial mats in terrestrial environments contributing to early signals of oxidative weathering (Stüeken et al., 2012; Lalonde and Konhauser, 2015).

CONCLUSIONS AND SIGNIFICANCE

Geochemical, petrographic, and sedimentary data from 2.7 Ga Hartbeesfontein stromatolites support the evolution of oxygenic photosynthesis at least 300 m.y. before the GOE, which substantiates previous evidence from non-biogenic sedimentary deposits and molecular clocks. Localized oxygenic photosynthesis in lacustrine stromatolites also strengthens hypotheses of non-marine benthic mats as oxygen oases before the GOE, as predicted by geochemical models, observations of modern microbial mats, and phylogenetic analyses of cyanobacteria. The presence of sub-meter–scale oxygen oases at ca. 2.7 Ga helps to reconcile previous Neoarchean evidence for localized, oxidative continental weathering under a reducing atmosphere.

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REFERENCES CITED

Barrat, J.A., Boulègue, J., Tiercelin, J.J., and Lesourd, M., 2000, Strontium isotopes and rare-earth element geochemistry of hydrothermal carbonate deposits from Lake Tanganyika, East Africa: Geochimica et Cosmochimica Acta, v. 64, p. 287–298, https://doi.org/10.1016/S0016-7037(99)00294-X.

Bau, M., and Dulski, P., 1996, Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa: Precambrian Research, v. 79, p. 37–55, https://doi.org/10.1016/0301-9268(95)00087-9.

Bolhar, R., and van Kranendonk, M., 2007, A non-marine depositional setting for the northern Fortescue Group, Pilbara Craton, inferred from trace element geochemistry of stromatolitic carbonates: Precambrian Research, v. 155, p. 229–250, https://doi.org/10.1016/j.precamres.2007.02.002.

Bonnand, P., Lalonde, S.V., Boyet, M., Heubeck, C., Homann, M., Nonnotte, P., Foster, I., Konhauser, K.O., and Köhler, I., 2020, Post-depositional REE mobility in a Paleoarchean banded iron formation revealed by La-Ce geochronology: A cautionary tale for signals of ancient oxygenation: Earth and

Planetary Science Letters, v. 547, https://doi.org/10.1016/j.epsl.2020.116452.
Bosak, T., Liang, B., Sim, M.S., and Petroff, A.P., 2009, Morphological record of oxygenic photosynthesis in conical stromatolites: Proceedings of the National Academy of Sciences of the United States of America, v. 106, p. 10,939–10,943, https://doi.org/10.1073/pnas.0900885106.
Bosak, T., Bush, J.W.M., Flynn, M.R., Liang, B., Ono, S., Petroff, A.P., and Sim, M.S., 2010, Formation and stability of oxygen-rich bubbles that shape photosynthetic mats: Formation and stability of oxygen-rich bubbles: Geobiology, v. 8, p. 45–55, https://doi.org/10.1111/j.1472-4669.2009.00227.x.
Buick, R., 1992, The antiquity of oxygenic photosynthesis: Evidence from stromatolites in sulphate-deficient Archaean lakes: Science, v. 255, p. 74–77, https://doi.org/10.1126/science.11536492.
Byrne, R.H., and Sholkovitz, E.R., 1996, Marine chemistry and geochemistry of the lanthanides, *in* Gschneidner, K.A., Jr., and Eyring, L., eds., Handbook on the Physics and Chemistry of Rare Earths: Elsevier, v. 23, p. 497–593, https://doi.org/10.1016/S0168-1273(96)23009-0.
Crow, C., and Condie, K.C., 1988, Geochemistry and origin of late Archean volcanics from the Ventersdorp Supergroup, South Africa: Precambrian Research, v. 42, p. 19–37, https://doi.org/10.1016/0301-9268(88)90008-3.
De Carlo, E.H., Wen, X.-Y., and Irving, M., 1997, The influence of redox reactions on the uptake of dissolved Ce by suspended Fe and Mn oxide particles: Aquatic Geochemistry, v. 3, p. 357–389, https://doi.org/10.1023/A:1009664626181.
Derry, L.A., and Jacobsen, S.B., 1990, The chemical evolution of Precambrian seawater: Evidence from REEs in banded iron formations: Geochimica et Cosmochimica Acta, v. 54, p. 2965–2977, https://doi.org/10.1016/0016-7037(90)90114-Z.
Farquhar, J., 2000, Atmospheric influence of Earth's earliest sulfur cycle: Science, v. 289, p. 756–758, https://doi.org/10.1126/science.289.5480.756.
Fischer, W.W., Hemp, J., and Johnson, J.E., 2016, Evolution of oxygenic photosynthesis: Annual Review of Earth and Planetary Sciences, v. 44, p. 647–683, https://doi.org/10.1146/annurev-earth-060313-054810.
German, C.R., Holliday, B.P., and Elderfield, H., 1991, Redox cycling of rare earth elements in the suboxic zone of the Black Sea: Geochimica et Cosmochimica Acta, v. 55, p. 3553–3558, https://doi.org/10.1016/0016-7037(91)90055-A.
Glasby, G.P., Gwozdz, R., Kunzendorf, H., Friedrich, G., and Thijssen, T., 1987, The distribution of rare earth and minor elements in manganese nodules and sediments from the equatorial and S.W. Pacific: Lithos, v. 20, p. 97–113, https://doi.org/10.1016/0024-4937(87)90001-6.
Hao, J., Knoll, A.H., Huang, F., Schieber, J., Hazen, R.M., and Daniel, I., 2020, Cycling phosphorus on the Archean Earth: Part II. Phosphorus limitation on primary production in Archean ecosystems: Geochimica et Cosmochimica Acta, v. 280, p. 360–377, https://doi.org/10.1016/j.gca.2020.04.005.
Hayashi, T., Tanimizu, M., and Tanaka, T., 2004, Origin of negative Ce anomalies in Barberton sedimentary rocks, deduced from La–Ce and Sm–Nd isotope systematics: Precambrian Research, v. 135, p. 345–357, https://doi.org/10.1016/j.precamres.2004.09.004.
Hoehler, T.M., Bebout, B.M., and Des Marais, D.J., 2001, The role of microbial mats in the production of reduced gases on the early Earth: Nature, v. 412, p. 324–327, https://doi.org/10.1038/35085554.
Holland, H.D., 2002, Volcanic gases, black smokers, and the great oxidation event: Geochimica et Cosmochimica Acta, v. 66, p. 3811–3826, https://doi.org/10.1016/S0016-7037(02)00950-X.
Kamber, B.S., Bolhar, R., and Webb, G.E., 2004, Geochemistry of late Archaean stromatolites from Zimbabwe: Evidence for microbial life in restricted epicontinental seas: Precambrian Research, v. 132, p. 379–399, https://doi.org/10.1016/j.precamres.2004.03.006.
Karpeta, W.P., 1989, Bedded cherts in the Rietgat Formation, Hartbeesfontein, South Africa; a late Archaean to early Proterozoic magadiitic alkaline playa lake deposit?: South African Journal of Geology, v. 92, p. 29–36.
Kasting, J.F., 1991, Box models for the evolution of atmospheric oxygen: An update: Global and Planetary Change, v. 5, p. 125–131, https://doi.org/10.1016/0921-8181(91)90133-H.
Kump, L.R., and Barley, M.E., 2007, Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago: Nature, v. 448, p. 1033–1036, https://doi.org/10.1038/nature06058.
Lalonde, S.V., and Konhauser, K.O., 2015, Benthic perspective on Earth's oldest evidence for oxygenic photosynthesis: Proceedings of the National Academy of Sciences of the United States of America, v. 112, p. 995–1000, https://doi.org/10.1073/pnas.1415718112.
Lawrence, M.G., and Kamber, B.S., 2006, The behaviour of the rare earth elements during estuarine mixing—revisited: Marine Chemistry, v. 100, p. 147–161, https://doi.org/10.1016/j.marchem.2005.11.007.
Mata, S.A., Harwood, C.L., Corsetti, F.A., Stork, N.J., Eilers, K., Berelson, W.M., and Spear, J.R., 2012, Influence of gas production and filament orientation on stromatolite microfabric: Palaios, v. 27, p. 206–219, https://doi.org/10.2110/palo.2011.p11-088r.
Olson, S.L., Kump, L.R., and Kasting, J.F., 2013, Quantifying the areal extent and dissolved oxygen concentrations of Archean oxygen oases: Chemical Geology, v. 362, p. 35–43, https://doi.org/10.1016/j.chemgeo.2013.08.012.
Planavsky, N.J., Robbins, L.J., Kamber, B.S., and Schoenberg, R., 2020, Weathering, alteration and reconstructing Earth's oxygenation: Interface Focus, v. 10, https://doi.org/10.1098/rsfs.2019.0140.
Raudsepp, M.J., 2012, Late Archean oceans: A laboratory model of oxygen oases [M.S. thesis]: Ontario, Canada, University of Western Ontario, 172 p.
Riding, R., Fralick, P., and Liang, L., 2014, Identification of an Archean marine oxygen oasis: Precambrian Research, v. 251, p. 232–237, https://doi.org/10.1016/j.precamres.2014.06.017.
Sholkovitz, E.R., Landing, W.M., and Lewis, B.L., 1994, Ocean particle chemistry: The fractionation of rare earth elements between suspended particles and seawater: Geochimica et Cosmochimica Acta, v. 58, p. 1567–1579, https://doi.org/10.1016/0016-7037(94)90559-2.
Slotznick, S.P., Johnson, J.E., Rasmussen, B., Raub, T.D., Webb, S.M., Zi, J.-W., Kirschvink, J.L., and Fischer, W.W., 2022, Reexamination of 2.5-Ga "whiff" of oxygen interval points to anoxic ocean before GOE: Science Advances, v. 8, https://doi.org/10.1126/sciadv.abj7190.
Stüeken, E.E., Catling, D.C., and Buick, R., 2012, Contributions to late Archaean sulphur cycling by life on land: Nature Geoscience, v. 5, p. 722–725, https://doi.org/10.1038/ngeo1585.
Sumner, D.Y., Hawes, I., Mackey, T.J., Jungblut, A.D., and Doran, P.T., 2015, Antarctic microbial mats: A modern analog for Archean lacustrine oxygen oases: Geology, v. 43, p. 887–890, https://doi.org/10.1130/G36966.1.
Wilmeth, D.T., Corsetti, F.A., Beukes, N.J., Awramik, S.M., Petryshyn, V., Spear, J.R., and Celestian, A.J., 2019, Neoarchean (2.7 Ga) lacustrine stromatolite deposits in the Hartbeesfontein Basin, Ventersdorp Supergroup, South Africa: Implications for oxygen oases: Precambrian Research, v. 320, p. 291–302, https://doi.org/10.1016/j.precamres.2018.11.009.

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