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Short communication

Identification of an Archean marine oxygen oasis

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ABSTRACT

The early Earth was essentially anoxic. A number of indicators suggest the presence of oxygenic photosynthesis ~2700–3000 million years (Ma) ago, but direct evidence for molecular oxygen (O_2) in seawater has remained elusive. Here we report rare earth element (REE) analyses of ~2800 million year old shallow-marine limestones and deep-water iron-rich sediments at Steep Rock Lake, Canada. These show that the seawater from which extensive shallow-water limestones precipitated was oxygenated, whereas the adjacent deeper waters where iron-rich sediments formed were not. We propose that oxygen promoted limestone precipitation by oxidative removal of dissolved ferrous iron species, Fe(II), to insoluble Fe(III) oxyhydroxide, and estimate that at least 10.25 μM oxygen concentration in seawater was required to accomplish this at Steep Rock. This agrees with the hypothesis that an ample supply of dissolved Fe(II) in Archean oceans would have hindered limestone formation. There is no direct evidence for the oxygen source at Steep Rock, but organic carbon isotope values and diverse stromatolites in the limestones suggest the presence of cyanobacteria. Our findings support the view that during the Archean significant oxygen levels first developed in protected nutrient-rich shallow marine habitats. They indicate that these environments were spatially restricted, transient, and promoted limestone precipitation. If Archean marine limestones in general reflect localized oxygenic removal of dissolved iron at the margins of otherwise anoxic iron-rich seas, then early oxygen oases are less elusive than has been assumed.

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1. Introduction

Progressive oxygenation of the atmosphere and hydrosphere had a major long-term effect on Earth-surface environments and the development of life. Its inception is widely attributed to the development of oxygenic photosynthesis by cyanobacteria during the Archean (Canfield, 2005, Holland, 2006). The existence of oxygenic photosynthesis ~2700 to 3000 Ma ago (Canfield, 2005; Nisbet et al., 2007; Buick, 2008; Schwartzman et al., 2008; Schopf, 2011) is suggested by chromium isotopes and redox-sensitive metals in 2920–2980 Ma sediments (Crowe et al., 2013), very negative carbon isotope values 2760 Ma ago that suggest methane oxidation (Hayes, 1994), phototrophic filaments in 2720 Ma stromatolites (Buick, 1992), hydrocarbon biomarkers for oxygenic photosynthetic cyanobacteria at 2720–2560 Ma (Eigenbrode et al., 2008), and correlated iron and molybdenum isotope compositions in 2680 Ma sediments (Czaja et al., 2012). Much of the early free oxygen (O_2) is thought to have been removed by reaction

with dissolved iron in seawater, contributing to widespread deposition of deep water iron- and silica-rich banded iron formation (Canfield, 2005; Holland, 2006). Nonetheless, substantial amounts of molecular oxygen might have accumulated locally in protected shallow-water environments that favored cyanobacterial productivity (MacGregor, 1927; Cloud, 1965; Kasting, 1992) and were sufficiently isolated so that the oxygen was not all immediately scavenged (Hayes, 1983). With a low rate of atmospheric exchange, O_2 levels in these 'oxygen oases' (Fischer, 1965) could have approached 0.016 atm (0.08 PAL), even under an anoxic atmosphere (Kasting, 1992; Pavlov and Kasting, 2002; Olson et al., 2013).

2. Steep Rock

We collected samples from ~2800 Ma (Fralick et al., 2008) limestones at Steep Rock Lake, 5 km north of Atikokan, Northwestern Ontario, in the central Wabigoon Subprovince of the Canadian Shield (Supplemental Data). This 500 m thick (Fig. 1) unit of calcium carbonate ($CaCO_3$) was chosen for study as the biogenic structures are well preserved (Wilks and Nisbet, 1988) and there is little evidence of chemical alteration (Veizer et al., 1982). The succession was deposited on an oceanic, volcanic plateau (Fralick et al., 2008)
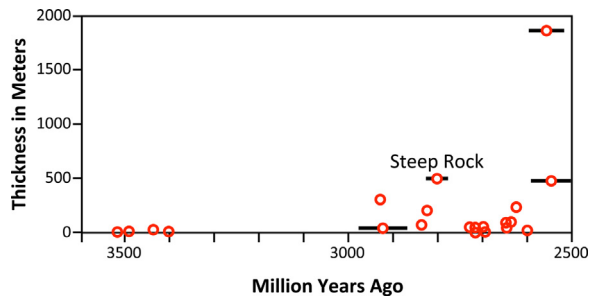
Fig. 1. Thickness-age plot of sedimentary calcium and magnesium carbonate rock units older than 2500 Ma (see Supplemental Data for details). Age error bars are horizontal.

and is laterally and vertically transitional to iron formation (Fig. 2). It overlies ~3000 Ma tonalitic gneiss eroded by a paleo-channel network back-filled with fluvial sandstones and conglomerates (Wilks and Nisbet, 1988; Fralick et al., 2008). These were covered by a transgressing sea that deposited dominantly $CaCO_3$, with thin layers of dolomite [$CaMg(CO_3)_2$], ankerite [$Ca(Fe,Mg(CO_3)_2$], and siderite ($FeCO_3$) that variously formed as primary, and as early and late diagenetic, products. The Steep Rock carbonate deposit therefore occupied a shallow platform environment adjacent to deeper water. Various morphologies, including columnar and domical forms, of relatively small (<0.5 m thick) crinkly laminated stromatolites that closely resemble lithified microbial mats occur in the lower part of the limestone (Wilks and Nisbet, 1985), and the upper part is dominated by large domes up to 5 m across composed of interlayered fenestral fabrics, interpreted as microbial, and crystal fan layers, that formed as aragonite seafloor precipitates (Sumner and Grotzinger, 2000) (Fig. 3). Manganese- and iron-oxide deposits ('Paint Rock') directly overlie the limestone (Wilks and Nisbet, 1988; Fralick et al., 2008). Steep Rock limestone formation was terminated as relative sea level rose and the platform was covered by these deeper water manganese and iron deposits (Fralick et al., 2008).

3. Methods

Nine samples of iron formation and 23 samples of limestone were selected to be representative of the succession and lithotypes present. Each sample was cut from a single fabric component, then hand crushed and as much of the white blocky cement as possible was removed before final crushing. The samples were analyzed for rare earth elements (REE) by inductively coupled plasma mass spectrometry (ICP-MS) at the Instrumentation Laboratory at Lakehead University. Calcium was analyzed by ICP-AES at the same facility using the same sample preparation techniques. For these analyses, 500 mg aliquots of powder were digested by a five-stage procedure involving initial release of the volatile phase using dilute hydrochloric acid, followed by three separate treatments with nitric and hydrofluoric acid separated by periods of drying. Finally, the sample was dissolved in dilute nitric acid and diluted 1000 times. Strontium was analyzed at the Geoscience Laboratories of the Ontario Ministry of Northern Development and Mines in Sudbury, Ontario. Two hundred milligram aliquots of powder were digested by a two-stage procedure involving initial decomposition in a closed beaker by a mixture of HF with lesser amounts of HCl and $HClO_4$ followed by a second mixture of dilute HCl and $HClO_4$. For REE, Sr and Ca analyses, blanks and appropriate standards were run with the samples. Accuracy and precision were evaluated by analyzing duplicate samples and the standard reference materials imbedded in the run, and were within acceptable limits. The REE data were standardized to post-Archean Australian Shale. The nine samples of iron formation showed no significant difference in REE pattern shape between the various sample lithologies. A limestone sample from the base of the formation contained sufficient siliciclastic material for this component to dominate its REE pattern, and it is plotted as a siliciclastic with two shale samples from the iron formation (Fig. 4).

To validate the presence of negative Ce anomalies we conducted sample treatment, analyzed comparative samples, and analyzed samples using a different laboratory, as follows. Two samples (SR22A, SR16A) were selected for different analytical treatment. A partial digestion using 5% acetic acid was performed on sample SR22A, followed by desiccation of the liquid, dissolution in 2% nitric acid and analysis of REEs on an ICP-MS at Lakehead University (Fig. 5a). Four samples from the Paleoproterozoic Gunflint Formation, with REE abundances lower than SR22A, were also analyzed. To bring the abundances in solution to well above detection limits, the dilution was limited to fifty times. The four Gunflint samples showed no significant negative Ce anomaly, whereas SR22A had an obvious negative Ce anomaly (Fig. 5a). The REE concentrations
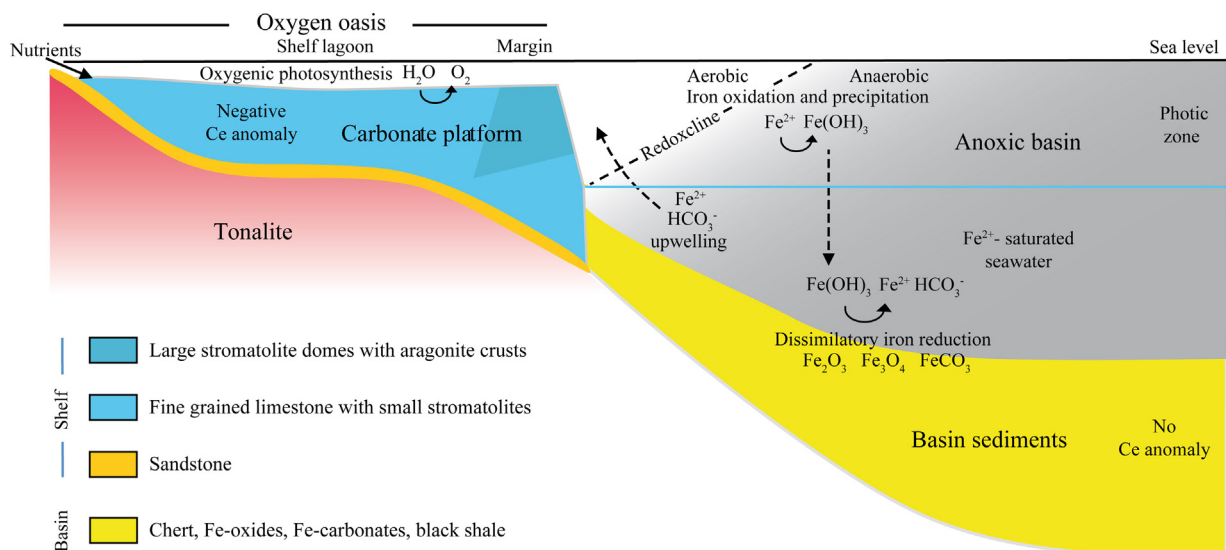

Fig. 2. Interpretive cross-section of Steep Rock oxygenated carbonate platform and adjacent anoxic and iron-rich basin, showing inferred stratigraphic relationships, conditions, and microbial metabolic processes (not to scale).
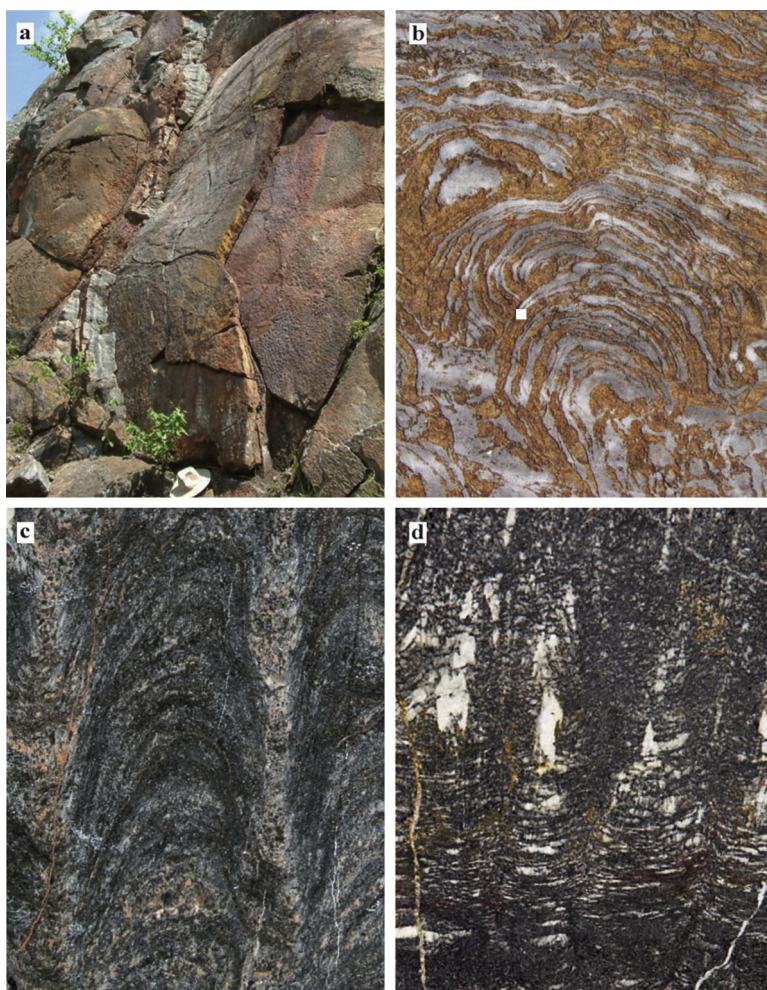
Fig. 3. Steep Rock stromatolites and associated limestone fabrics; see Supplemental Data for locality details. (a) Steeply dipping large, current-orientated, domical stromatolites at the platform margin; dome above hat is ~5 m long. The domes consist of alternating dark and light gray centimetric layers respectively composed of crystal fan crust, interpreted as originally aragonite, and cuspate fenestral fabric interpreted as microbial, and combinations of these two fabrics (see d). Wilks #4 locality. (b) Small irregularly laminated superimposed domical stromatolites, with layers emphasized by iron carbonate; width of view ~5 cm. Wilks #3 locality. (c) Small closely spaced columnar stromatolites with enveloping irregular laminae that frequently cross narrow inter-column spaces; width of view ~5 cm. Wilks #3 locality. (d) Cuspate fenestral fabric composed of nested irregular concave-up fenestrae, filled by white sparry calcite, that grade upward into and are overprinted by subvertical crystal fans interpreted as originally aragonite; width of view ~6 cm. Wilks #3 locality.

in sample SR16A were analyzed by laser ablation ICP-MS at the University of Bremen, Germany. The eleven spots analyzed are averaged in Fig. 5b. All spots showed significant negative Ce anomalies. The shapes of the curves and the pronounced negative Ce anomalies in samples SR22A and SR16A are very similar (Fig. 5), even though quite different analytical techniques were used.

To estimate the dissolved oxygen level required to precipitate calcium carbonate minerals at Steep Rock we first calculated the ferrous iron concentration, assuming that siderite was in equilibrium with aragonite in Archean seawater containing 10–30 mmol/l of Ca^{2+} (Canfield, 2005) at temperatures of 15–40 °C (Hren et al., 2009; Rosing et al., 2010). Under this condition, siderite and aragonite may co-precipitate, but calcite is inhibited by the presence of ferrous iron. To remove ferrous iron inhibition for calcite, we assumed that oxidative removal of Fe(II) occurred. The minimum amount of Fe(II) to be oxidized is thus equal to the difference between this equilibrium concentration and the concentration that inhibits calcite precipitation. We used 10 μM ferrous iron as the inhibition level, based on previous results that calcite rather than aragonite precipitated when Fe^{2+} was <10 μM (Herzog et al., 1989). The dissolved O_2 was calculated assuming 4 moles of electrons from Fe oxidation can be taken up by each mole of O_2.

4. Results and discussion

4.1. Rare earth elements

A variety of distinct and relatively well-preserved limestone components, including crystal fans that were originally aragonite, cuspate fenestral fabric, and various stromatolites, were analyzed for REE concentrations (Supplemental Data). Oxide, sulfide and carbonate iron formation, together with chert and fine-grained siliciclastic sediment from the deeper water facies were also analyzed.

In a detailed comparison of the alteration of Archean carbonate units, Veizer et al. (1982) found that the Steep Rock limestone was among the least altered of the fourteen major carbonate bearing rock successions sampled. In the present study, we found that samples from adjacent (on the mm-scale), fenestra-dominated areas (SR-5A and 8-24A) and blocky white cement-dominated areas (SR-5B and 8-24B) (see Supplemental Table 2) have significantly different REE concentrations. This is likely a primary signature, since later alteration would homogenize REE abundances. Carbon and oxygen stable isotopes measured in twenty-three of our limestone samples had values similar to other Archean carbonate units, $\delta^{13}C = 1.8 \pm 0.6‰$ PDB and $\delta^{18}O = 21.4 \pm 1.6‰$ SMOW. The
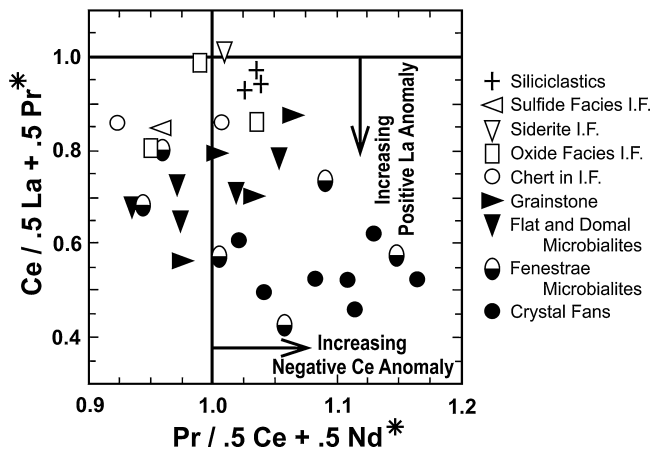
Fig. 4. Plot of the REE La anomaly, *Y* axis, against the Ce anomaly, *X* axis. Samples plotting below 0.95 or above 1.05 are considered to have significant anomalies. The iron formation samples plot closer to the 1, 1 intercept than the carbonate samples. Crystal fans and some fenestral microbialites interlayered with these crystal fans have significant negative Ce anomalies. This indicates that the seawater they precipitated from had previously encountered high enough oxygen levels to cause some of the Ce to leave the solution in that area, imparting a negative Ce anomaly to the seawater. The asterisk indicates the elements are Post-Archean Australian Shale normalized.

Archean Campbellrand carbonates of South Africa have a $\delta^{13}C$ of 0.5‰ and a $\delta^{18}O$ of 22‰ (Fischer et al., 2009), whereas the Kuruman Iron Formation in the Campbellrand has a $\delta^{18}O$ of 21‰ (Heimann et al., 2010). In Western Australia, dolostones of the Hamersley have $\delta^{13}C$ of 0 ± 1.2‰ and $\delta^{18}O$ of 21‰ (Veizer et al., 1990). The Dales Gorge and Brockman iron formations of the Hamersley have $\delta^{18}O$ of approximately 19.5‰ (Kaufman et al., 1990). The most common interpretation of the stable isotope results summarized here is that they preclude extensive water rock interaction or fractionation during metamorphism. Strontium isotopic values for the Steep Rock limestones of 0.7020, with none of the six samples analyzed being above 0.7025 (Veizer et al., 1989), support this view. These ratios are inferred to be similar to those of Archean seawater at approximately this time, based on 0.7030 determined for Pongola Supergroup limestones (Eglington et al., 2003). The strontium isotopic ratios obtained for Steep Rock samples may also help explain the discrepancy in REE abundances between those reported here and those obtained by Planavsky and Murphy (2007) and Planavsky et al. (2010), who detected no negative Ce anomalies at Steep Rock. The $^{87}Sr/^{86}Sr$ ratio of Steep Rock limestones (0.7020) is markedly different than the ratio for Steep Rock dolomites (0.7080), whose value is similar to secondary carbonate in Steep Rock tectonic breccias (Veizer et al., 1989). Planavsky et al. (2010) categorize the majority of their samples as calcite/dolomite.

Four samples we analyzed that contained a significant amount of secondary dolomite yielded flat Ce abundances, similar to those of Planavsky et al. (2010). Steep Rock samples containing significant dolomite should therefore be avoided for REE analysis, since their Sr isotopic concentrations suggest they have undergone extensive alteration. However, another possible explanation of the discrepancy is that the samples in Planavsky et al. (2010) did not come from the same area as our samples with negative Ce anomalies. Samples in our dataset from the area that Planavsky et al. (2010) sampled have similar patterns to their samples. This sample area is in the lower part of the formation. It is some, but not all, of the samples we obtained from the upper part of the Steep Rock limestone that exhibit the negative Ce anomaly. A significant negative cerium anomaly that is present in eight of the limestone samples is absent from the adjacent deeper water iron formation samples (Fig. 4) and from the stromatolite and microbialite samples lower in the Steep Rock limestone. Cerium is the only REE with a 4+ valence state, in which it forms an insoluble oxide and is removed from solution. The negative anomaly indicates that the seawater from which the limestone precipitated had encountered sufficient oxygen to remove cerium, whereas water during initial flooding of the platform, and water seaward of the shallow portion of the platform, had not.

4.2. Archean seawater chemistry

Limestone deposition at Steep Rock, as well as at localities of similar age in southern Africa, has been attributed to increased seawater pH due to cyanobacterial primary productivity that lowered aquatic CO_2 concentrations (Nisbet et al., 2007). However, even at circumneutral to alkaline pH, the abundance of dissolved ferrous ion, Fe^{2+}, in anoxic Archean seawater (Canfield, 2005; Holland, 2006) would have remained an obstacle to $CaCO_3$ precipitation by favoring the less soluble ferrous carbonate (siderite) (Stumm and Morgan, 1996; Sumner, 1997). Substantial amounts of Fe^{2+} would have had to be removed from seawater to promote Ca-carbonate precipitation. Oxygen, indicated by our REE analyses, could have accomplished this by oxidizing Fe(II) species to insoluble Fe(III) (Sumner and Grotzinger, 1996; Sumner, 2002; Canfield, 2005; Holland, 2006). We infer that Steep Rock limestone directly reflects the redox condition of the shallow seawater from which it precipitated and that the limestone formed in shallow suboxic/oxic seawater above a laterally bordering redoxcline (Fig. 2). Similar circumstances have been suggested for ~2600–2520 Ma shallow-water Ca- and Mg-carbonates associated with deep water iron deposits in South Africa (Sumner, 1997; Klein and Beukes, 1989).

Steep Rock limestones are now calcite but preserve evidence suggesting the initial presence of both aragonite and calcite (Supplemental Data). Occurrence of both these $CaCO_3$ minerals in the same succession would permit estimation of the minimum level
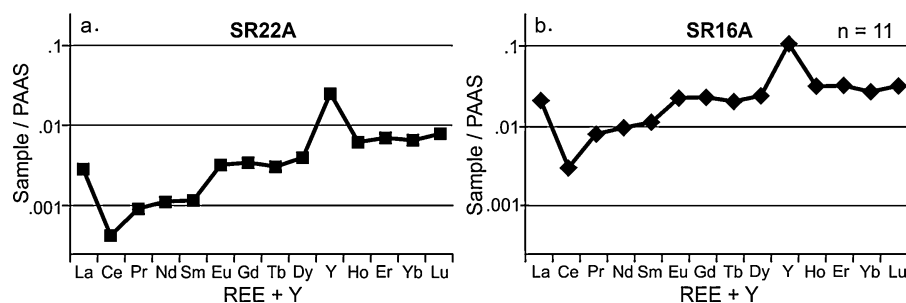

Fig. 5. Comparison of Rare Earth Element plus *Y* plots, normalized to post-Archean Australian shale, for two Steep Rock samples selected for different analytical treatment. (a) Sample SR22A, prepared by partial dissolution with 5% acetic acid, followed by 50× dilution to increase the concentration of the elements in solution. Note the pronounced negative Ce anomaly. (b) Sample SR16A, analyzed by LA-ICP-MS. This curve is the average of 11 analyses of sample SR 16A, all of which show the negative Ce anomaly. Note similarity in the shape of the curve to that in A.

of dissolved oxygen in the seawater from which they precipitated. Our reasoning is as follows. Fe^{2+} concentrations that only slightly affect aragonite precipitation can completely inhibit calcite (Herzog et al., 1989). Consequently, during progressive removal of ferrous iron from iron-rich seawater, precipitation of siderite should be succeeded first by aragonite precipitation and then, with further oxidative removal of Fe^{2+}, by calcite precipitation. Based on averages of current assessments of Archean seawater calcium concentrations (Veizer et al., 1982) and temperatures (Hren et al., 2009; Rosing et al., 2010), aragonite would have been favored over siderite when concentration of Fe^{2+} was below 51 μM, and calcite over aragonite when Fe^{2+} was <10 μM (Herzog et al., 1989). It follows that precipitation of calcite under the aragonite-siderite equilibrium condition would have required oxidative removal of at least 41 μM Fe^{2+}. Accomplishing this with molecular O_2 would have required at least 10.25 μM of O_2, approximately equivalent to 0.06 PAL (Supplemental Data). This minimum estimate of required O_2 concentration at Steep Rock is within the range of up to 0.08 PAL of O_2 that could accumulate in localized Archean environments under an essentially anoxic atmosphere (Kasting, 1992; Pavlov and Kasting, 2002). This result is also consistent with a recent calculation using a quasi-3D model that predicted 1–10 μM of O_2 in somewhat more realistic oxygen oases (Olson et al., 2013).

4.3. Marine oxygenation

Previous inference of oxygenic photosynthesis at Steep Rock was based on organic carbon isotope values in the range −30.6‰ to −21.6‰ (Grassineau et al., 2006). However, similar values can be produced by anoxygenic photosynthesis (Des Marais, 2001), as noted for much older Archean samples (Schopf, 2011). Although these carbon isotope values are not conclusive indicators they are consistent with oxygenic photosynthesis at Steep Rock (Nisbet et al., 2007), as is the presence of diverse stromatolites (Wilks and Nisbet, 1988) and cuspate fenestral fabric (Sumner, 1997) whose microbial communities could have included cyanobacteria. Accumulation of black shales with up to 15 wt% carbon in deeper water iron formation adjacent to the Steep Rock limestone also suggests a productive phytoplankton community consistent with cyanobacteria. Deposition of manganese oxide-bearing 'Paint Rock' above the limestone indicates oxygenation (Nisbet et al., 2007) that was probably weak during the terminal stage of the oasis, as

iron- and manganese-rich waters drowned the carbonate platform (Fig. 6). More widespread indicators of incipient marine oxygenation ~2800 Ma ago include chromium isotope values in iron formation (Frei et al., 2009) and very negative (≤−60‰) organic carbon isotope values, some from Steep Rock (Hayes, 1994), that suggest bacterial methane oxidation (Hayes, 1983, 1994) which would have required oxygen or oxidized compounds. Sedimentary structures suggest the presence of cyanobacterial mats 2900 Ma ago (Noffke et al., 2008), and probable terrestrial oxidation of pyrite (Stüeken et al., 2012) is also consistent with incipient marine oxygenation 2700–2800 Ma ago. Contemporaneous atmospheric oxygen levels may have remained quite low (Wille et al., 2013). Atmospheric oxygen concentrations of at least 6×10^{-5} PAL, and possibly as high as 3×10^{-3} PAL, are estimated from Cr-isotopes and trace metals in 2.92–2.98 Ga sediments in South Africa (Crowe et al., 2013). These values, equivalent to 0.00006 and 0.003 PAL respectively, are at least 20 times below the minimum level of oxygen that we estimate to enable Ca-carbonate precipitation in Steep Rock seawater.

5. Conclusions

The formation of Archean marine limestones resulted from oxidative iron-removal by oxygen, presumably produced by cyanobacteria. Oxygen oases developed in nutrient-rich shallow shelf seas that promoted cyanobacterial growth and whose isolation from open marine circulation limited replenishment of removed iron. As a result, limestones accumulated in these oxygen oases, forming the earliest marine carbonate platforms (Fralick and Riding, 2012). The ~2800 Ma Steep Rock limestone is an example of this. The development of oxygen oases in protected marginal marine environments was predicted (Fischer, 1965; Hayes, 1983; Kasting, 1992) but their profound effect on $CaCO_3$ precipitation was not fully appreciated. We propose that Archean marine limestones are a proxy for oxygenation. This interpretation is supported by the presence of REE values at Steep Rock indicating oxygenation. Near the Steep Rock platform margin, subject to incursion of iron-rich water, aragonite precipitated. In the platform interior, increased iron-removal allowed calcite to precipitate. In contrast, Archean non-marine limestones precipitating from iron-poor waters could have formed in the absence of oxygen. Assuming long-term accumulation rates similar to those of tropical carbonates of the past 500 Ma (Schlager, 2003), Steep Rock platform could have persisted for at least 5 Ma before it was inundated by sub-oxic and anoxic seawater and covered by manganese- and then iron-rich sediments (Fig. 6). We infer that Steep Rock, and similar carbonate platforms at the margins of otherwise anoxic iron-rich seas, reflect an early, transient stage in the evolution of Earth surface environments as oxygenation began its advance that, ultimately, would overwhelm atmosphere and oceans alike.
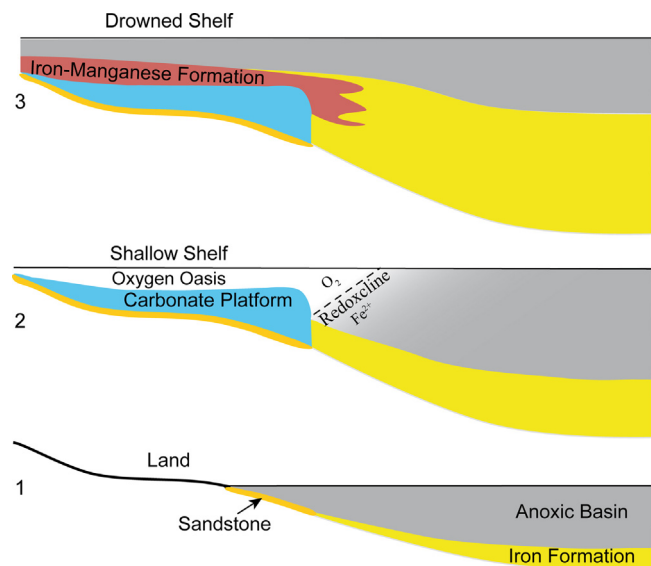
Fig. 6. Interpretive cross-sections showing environments inferred at Steep Rock, before (1), during (2) and after (3) oxygen 'oasis' development.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.precamres. 2014.06.017.

References

Buick, R., 1992. The antiquity of oxygenic photosynthesis: evidence from stromatolites in sulfate-deficient Archaean lakes. Science 255, 74–77.

Buick, R., 2008. When did oxygenic photosynthesis evolve? Phil. Trans. R. Soc. B 363, 2731–2743.

Canfield, D.E., 2005. The early history of atmospheric oxygen: homage to Robert M Garrels. Annu. Rev. Earth Planet. Sci. 33, 1–36.

Cloud Jr., P.E., 1965. Significance of the Gunflint (Precambrian) microflora. Science 148, 27–35.

Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R., Canfield, D.E., 2013. Atmospheric oxygenation three billion years ago. Nature 501, 535–539.

Czaja, A.D., Johnson, C.M., Roden, E.E., Beard, B.L., Voegelin, A.R., Nägler, T.F., Beukes, N.J., Wille, M., 2012. Evidence for free oxygen in the Neoarchean ocean based on coupled iron–molybdenum isotope fractionation. Geochim. Cosmochim. Acta 86, 118–137.

Des Marais, D.J., 2001. Isotopic evolution of the biogeochemical carbon cycle during the Precambrian. Rev. Mineral. Geochem. 43, 555–578.

Eglington, B.M., Talma, A.S., Marais, S., Mathews, P.E., Dixon, J.G.P., 2003. Isotopic composition of Pongola Supergroup limestones from the Buffalo River George South Africa; constraints on their regional depositional setting. S. Afr. J. Geol. 106, 1–10.

Eigenbrode, J.L., Freeman, K.H., Summons, R.E., 2008. Methylhopane biomarker hydrocarbons in Hamersley Province sediments provide evidence for Neoarchean aerobiosis. Earth Planet. Sci. Lett. 273, 323–331.

Fischer, A.G., 1965. Fossils, early life, and atmospheric history. Proc. Natl. Acad. Sci. U.S.A. 53, 1205–1215.

Fischer, W.W., Schroeder, S., Lacassie, J.P., Beukes, N.J., Goldberg, T., Strauss, H., Horstmann, U.E., Schrag, D.P., Knoll, A.H., 2009. Isotopic constraints on the Late Archean carbon cycle from the Transvaal Supergroup along the western margin of the Kaapvaal Craton. S. Afr. Precambrian Res. 169, 15–27.

Fralick, P.W., Hollings, P., King, D., 2008. Stratigraphy, geochemistry and depositional environments of Mesoarchean sedimentary units in Western Superior Province: implications for generation of early crust. In: Condie, K.C., Pease, V. (Eds.), When did Plate Tectonics Begin on Planet Earth? Geol. Soc. Am. Special Paper 440, 77–96.

Fralick, P., Riding, R., 2012. Steep Rock carbonate platform: an early marine oxygen oasis. Goldschmidt 2012 Conference Abstracts. Mineral. Mag. 76, 1715.

Frei, R., Gaucher, C., Poulton, S.W., Canfield, D.E., 2009. Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. Nature 461, 250–253.

Grassineau, N., Abell, P., Appel, P.W.U., Lowry, D., Nisbet, E., 2006. Early life signatures in sulfur and carbon isotopes from Isua, Barberton Wabigoon (Steep Rock), and Belingwe Greenstone Belts (3.8 to 2.7 Ga). In: Kesler, S.E., Ohmoto, H. (Eds.), Evolution of Early Earth's Atmosphere, Hydrosphere, and Biosphere—Constraints from Ore Deposits. Geol. Soc. Am. 198, 33–52.

Hayes, J.M., 1983. Geochemical evidence bearing on the origin of aerobiosis, a speculative hypothesis. In: Schopf, J.W. (Ed.), Earth's Earliest Biosphere, Its Origin and Evolution. Princeton University Press, pp. 291–301.

Hayes, J.M., 1994. Global methanotrophy at the Archean–Proterozoic transition. In: Bengtson, S. (Ed.), Early life on Earth: Nobel Symposium No. 84. Columbia University Press, New York, pp. 220–236.

Heimann, A., Johnson, C.M., Beard, B.L., Valley, J.W., Roden, E.E., Spicuzza, M.J., Beukes, N.J., 2010. Fe, C, and O isotopic compositions of banded iron formation carbonates demonstrate a major role for dissimilatory iron reduction in approximately 2.5 Ga marine environments. Earth Planet. Sci. Lett. 294, 8–18.

Herzog, R.E., Shi, Q., Patil, J.N., Katz, J.L., 1989. Magnetic water treatment: the effect of iron on calcium carbonate nucleation and growth. Langmuir 5, 861–867.

Holland, H.D., 2006. The oxygenation of the atmosphere and oceans. Phil. Trans. R. Soc. B 361, 903–915.

Hren, M.T., Tice, M.M., Chamberlain, C.P., 2009. Oxygen and hydrogen isotope evidence for a temperate climate 3.42 billion years ago. Nature 462, 205–208.

Kasting, J.F., 1992. Models relating to Proterozoic atmospheric and oceanic chemistry. In: Schopf, J.W., Klein, C. (Eds.), The Proterozoic Biosphere, A Multidisciplinary Study. Cambridge University Press, Cambridge, UK, pp. 1185–1187.

Kaufman, A.J., Hayes, J.M., Klein, C., 1990. Primary and diagenetic controls of isotopic compositions of iron-formation carbonates. Geochim. Cosmochim. Acta 54, 3461–3473.

Klein, C., Beukes, N.J., 1989. Geochemistry and sedimentology of a facies transition from limestone to iron-formation deposition in the Early Proterozoic Transvaal Supergroup, South Africa. Econ. Geol. 84, 1733–1774.

MacGregor, A.R., 1927. The problem of the Precambrian atmosphere. S. Afr. J. Sci. 24, 155–172.

Nisbet, E.G., Grassineau, N.V., Howe, C.J., Abell, P.I., Regelous, M., Nisbet, R.E.R., 2007. The age of Rubisco: the evolution of oxygenic photosynthesis. Geobiology 5, 311–335.

Noffke, N., Beukes, N., Bower, D., Hazen, R.M., Swift, D.J.P., 2008. An actualistic perspective into Archean worlds — (cyano-)bacterially induced sedimentary structures in the siliciclastic Nhlazatse Section 2.9 Pongola Supergroup, South Africa. Geobiology 6, 5–20.

Olson, S.L., Kump, L.R., Kasting, J.F., 2013. Quantifying the areal extent and dissolved oxygen concentrations of Archean oxygen oases. Chem. Geol. 362, 35–43.

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

Planavsky, N., Bekker, A., Rouxel, O.J., Kamber, B., Hofmann, A., Knudsen, A., Lyons, T.W., 2010. Rare earth element and yttrium compositions of Archean and Paleoproterozoic Fe formations revisited: new perspectives on the significance and mechanisms of deposition. Geochim. Cosmochim. Acta 74, 6387–6405.

Planavsky, N., Murphy, J., 2007. Rare earth element patterns in Steep Rock carbonates: 53 Annual Meeting, Program with Abstracts, Institute on Lake Superior Geology, Proceedings, v. 53., pp. 59–60.

Rosing, M.T., Bird, D.K., Sleep, N.H., Bjerrum, C.J., 2010. No climate paradox under the faint early Sun. Nature 464, 744–747.

Schlager, W., 2003. Benthic carbonate factories of the Phanerozoic. Int. J. Earth Sci. 92, 445–464.

Schopf, J.W., 2011. The paleobiological record of photosynthesis. Photosynth. Res. 107, 87–101.

Schwartzman, D., Caldeira, K., Pavlov, A., 2008. Cyanobacterial emergence at 2.8 Gya and greenhouse feedbacks. Astrobiology 8, 187–203.

Stüeken, E.E., Catling, D.C., Buick, R., 2012. Contributions to late Archaean sulphur cycling by life on land. Nat. Geosci. 5, 722–725.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd ed. Wiley-Interscience, New York, pp. 1022.

Sumner, D.Y., 1997. Carbonate precipitation and oxygen stratification in late Archean seawater as deduced from facies and stratigraphy of the Gamohaan and Frisco formations, Transvaal Supergroup, South Africa. Am. J. Sci. 297, 455–487.

Sumner, D.Y., 2002. Decimetre-thick encrustations of calcite and aragonite on the sea-floor and implications for Neoarchean and Neoproterozoic ocean chemistry: Special Publications of the International Association of Sedimentologists, v. 33., pp. 107–120.

Sumner, D.Y., Grotzinger, J.P., 1996. Were kinetics of Archean calcium carbonate precipitation related to oxygen concentration? Geology 24, 119–122.

Sumner, D.Y., Grotzinger, J.P., 2000. Late Archean aragonite precipitation: petrography, facies associations, and environmental significance. In: Grotzinger, J.P., James, N.P. (Eds.), Carbonate Sedimentation and Diagenesis in the Evolving Precambrian World: SEPM, Special Publication, v. 67. , pp. 123–144.

Veizer, J., Clayton, R.N., Hinton, R.W., von Brunn, V., Mason, T.R., Buck, S.G., Hoefs, J., 1990. Geochemistry of Precambrian carbonates: 3 – shelf seas and non-marine environments of the Archean. Geochim. Cosmochim. Acta 54, 2717–2729.

Veizer, J., Compston, W., Hoefs, J., Nielson, H., 1982. Mantle buffering of the early oceans. Naturwissenschaften 69, 173–180.

Veizer, J., Hoefs, J., Lowe, D.R., Thurston, P.C., 1989. Geochemistry of Precambrian carbonates: II Archean greenstone belts and Archean seawater. Geochim. Cosmochim. Acta 53, 859–871.

Wilks, M.E., Nisbet, E.G., 1985. Archaean stromatolites from the Steep Rock Group, northwestern Ontario, Canada. Can. J. Earth Sci. 22, 792–799.

Wilks, M.E., Nisbet, E.G., 1988. Stratigraphy of the Steep Rock Group, northwest Ontario: a major Archaean unconformity and Archaean stromatolites. Can. J. Earth Sci. 25, 370–391.

Wille, M., Nebel, O., Van Kranendonk, M.J., Schoenberg, R., Kleinhanns, I.C., Ellwood, M.J., 2013. Mo–Cr isotope evidence for a reducing Archean atmosphere in 3.46–2.76 Ga black shales from the Pilbara, Western Australia. Chem. Geol. 340, 68–76.