An iodine record of Paleoproterozoic surface ocean oxygenation

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ABSTRACT

Constraining oxygen levels in the early Precambrian surface ocean has been a longstanding goal, but efforts have been challenged by the availability of suitable proxies. Here we present a novel approach, iodine geochemistry, which broadens our perspective by providing constraints on shallow, carbonate-dominated marine settings. Iodate (IO_3^-) persists exclusively in oxic waters and is the sole iodine species incorporated into carbonate minerals, allowing iodine-to-calcium ratios (I/Ca) in shallow carbonates to be used as a paleoredox indicator. Our data from a series of Mesoarchean through Paleoproterozoic carbonates deposited under shallow-marine conditions reveal a progressive surface ocean oxygenation in the early Paleoproterozoic. These data seem to indicate that a largely anoxic surface ocean extended throughout the Archean until the Great Oxidation Event (GOE) at ca. 2.4 Ga, implying that previous inferences of pre-GOE oxygen production may reflect oxygen oases, transient oxidation events, or oxygen levels below those required for IO_3^- accumulation. The data suggest formation and persistence of IO_3^- and, consequently, surface ocean oxygen concentrations of at least 1 µM during the GOE. Following the initial rise of oxygen, carbonate-associated iodine in globally extensive carbonate units deposited during the Lomagundi positive carbon isotope excursion at ca. 2.22–2.1 Ga suggests a widespread aerobic iodine cycle beyond that operating prior to the event, synchronous with high relative rates of organic carbon burial and apparent expansion of oxidative conditions.

INTRODUCTION

Measurements of iodine speciation in anoxic basins demonstrate that IO_3^- undergoes complete reduction to iodide (I^-) nearly simultaneously with O_2 depletion (Wong and Brewer, 1977; Emerson et al., 1979; Wong et al., 1985; Luther and Campbell, 1991). It was recently observed that during calcite precipitation, concentrations of carbonate-associated iodine increase linearly with those of IO_3^- in the precipitating medium, but I^- is completely excluded (Lu et al., 2010). Coupled with the well-known redox behavior of iodine, its seawater residence time of ~300 k.y. (Broecker et al., 1982), and concentrations near 450 nM in the modern ocean, this correlation suggests that I/Ca ratios in carbonates can be used as a robust indicator of the presence or absence of IO_3^-, and hence oxygen, in the water column. Further, post-depositional alteration of carbonates through diagenesis have been shown—if anything—to decrease the original I/Ca ratios (Loope et al., 2013), making post-depositional increases in I/Ca ratios highly unlikely.

Molybdenum and chromium geochemistry, each sensitive to aerobic manganese cycling, suggest mild and/or transient atmospheric oxygenation starting as early as 3.0 Ga (Crowe et al., 2013; Planavsky et al., 2014). Permanent accumulation of appreciable O_2 during the Great Oxidation Event (GOE) at roughly 2.3 Ga is further inferred from non–mass dependent sulfur isotope (NMD-S) fractionations (Bekker et al., 2004). However, constraints on surface ocean oxidation are limited both before and after the GOE, despite assumptions and mounting evidence that early oxygen was sourced from the marine photic zone following the advent of oxygenic photosynthesis 300–600 m.y. prior to the GOE (see Lyons et al., 2014). Here, we use a novel approach, I/(Ca + Mg) ratios in shallow-water carbonates, to determine the timing of the onset of marine aerobic iodine cycling and construct the first temporal record of early oxygen production specific to the surface ocean.

MATERIALS AND METHODS

I/(Ca + Mg) ratios were measured in 190 samples from 20 carbonate units ranging in age from 3.5 Ga to 1.9 Ga, with a focus on capturing the key periods of the earliest progressive oxygen expansion (Table 1). Magnesium is included to account for dolomitization, as all measured units are dolostones. Carbonates that experienced metamorphic temperatures greater than greenschist facies were not included in this study because previous work has shown significant iodine loss in shale at metamorphic temperatures of >400 °C (Muramatsu and Wedepohl, 1998). We generated fresh powders from carbonate samples to minimize the effects of weathering and surface contamination. Measurements of I, Ca, and Mg were performed on a quadrupole inductively coupled plasma–mass spectrometer (Bruker M90) at Syracuse University (New York, USA) according to the method of Lu et al. (2010). The precision of ^{127}I is typically better than 1% and is not reported separately for each sample. The standard deviation in counts per second (cps) for three blanks in a row is typically below 300 cps, while the sensitivity for 1 ppb standard is 80,000–120,000 cps. The detection limit for I/(Ca + Mg) is usually better than 0.1 µmol/mol, a value that loosely corresponds to 10 nM IO_3^- based on carbonate precipitation experiments by Lu et al. (2010).

RESULTS AND DISCUSSION

Archean

All carbonate samples predating ca. 2.45 Ga record iodine concentrations analytically indistinguishable from blank values (Fig. 1; Table 1),

TABLE 1. CARBONATES USED IN THIS STUDY AND PLOTTED IN FIGURE 1

Geologic Formation	Age (Ga)	n	Percent containing iodine
Dresser Fm., Warrawoona Group	ca. 3.5	8	0
Steep Rock Group	2.80–2.76	14	0
Tumbiana Fm., Fortescue Group	2.73–2.72	18	0
Cheshire Fm., Ngezi Group	2.65–2.55	3	0
Wittenoom Fm., Hamersley Group	2.56–2.50	16	0
Campbellrand Subgroup	2.56–2.54	6	0
Tongwane Fm., Chunniespoort Group	2.49–2.32	5	20
Duitschland Fm., Pretoria Group	2.49–2.32	2	0
Espanola Fm., Huronian Supergroup	2.48–2.32	8	0
Carbonates of Turee Creek Group	2.45–2.40	29	28
Gandarela Fm., Minas Supergroup	ca. 2.42	3	0
Gordon Lake Fm., Huronian Supergroup	2.32	9	11
Bad River Dolomite, Chocolay Group	2.32–2.22	2	0
Saunders Fm., Chocolay Group	2.32–2.22	1	0
Cercadinho Fm., Minas Supergroup	ca. 2.22	2	0
Lucknow Fm., Olifantshoek Group	2.15	5	80
Mcheka Fm., Lomagundi Group	2.15	37	95
Lower Albanel Fm., Mistassini Group	2.1	10	80
Aquas Claras Fm., Serra Pelada Sequence	2.1	8	50
Aluminum River Fm., Amer Group	1.95–1.91	4	0

Note: References to ages and data are available in Tables DR1 and DR2 (see text footnote 1).

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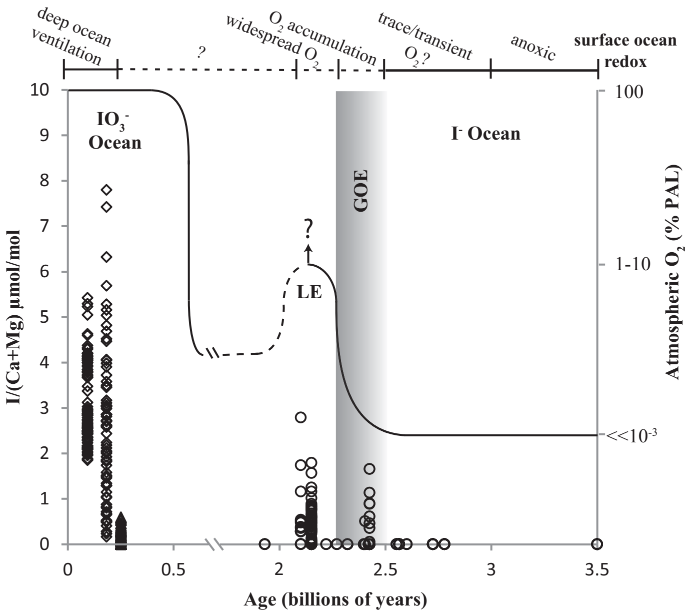

Figure 1. Compilation of all available I/(Ca + Mg) ratios through time. All ages are represented by the midpoint for ranges presented in Table 1. Data from Lu et al. (2010; diamonds), Loope et al. (2013; triangles), and this study (circles). Values from Lu et al. (2010) do not include Mg concentrations in the ratio, as these are for calcites. Oxygen curve generalized from Lyons et al. (2014). LE—Lomagundi Event; GOE—Great Oxidation Event; PAL—present atmospheric levels.

indicating I^- as the dominant inorganic iodine species in the water column. A lack of appreciable IO_3^- accumulation in the Archean shallow-marine carbonates suggests deposition under anoxic conditions. Overall, such a notion agrees well with significant NMD-S isotope signatures in the rock record until ca. 2.4 Ga (Bekker et al., 2004), constraining atmospheric oxygen concentrations to less than 10^{-5} of present atmospheric levels (Pavlov and Kasting, 2002). Though the sample set predating 2.5 Ga only includes six out of the 20 carbonates measured (Table 1), our work focuses on key units directly leading up to the GOE and some, such as the Tumbiana Formation, used for previous inferences of aerobiosis (Thomazo et al., 2011). Nevertheless, this limited sample scheme leaves open the possibility of surface ocean oxygen production beyond the resolution of our data. Regardless, the I/(Ca + Mg) record does not, at face value, support the idea of widespread, persistent surface ocean oxygen prior to the GOE.

Reservoir controls seem unlikely for the lack of carbonate-associated iodine prior to the GOE. Overall, the largest iodine sink in the modern ocean is organic matter (OM) burial, particularly via marine algae (Lu et al., 2010). Without effective sequestration with marine algae and other organisms, iodine would be more abundant in the ocean, as we observe for other hydrophilic halogens such as Br and Cl (Sharp and Draper, 2013). We propose that the absence of advanced marine algae and fewer biological sinks in the Archean would yield a seawater iodine reservoir much larger than today. Considering this, the first appearance of carbonate-associated iodine would be solely dependent on redox conditions allowing for IO_3^- production and accumulation from either I^- or intermediate forms.

For the Neoarchean, initially low I/(Ca + Mg) ratios, as would be expected if IO_3^- accumulated at only trace levels, may have been particularly vulnerable to diagenetic loss, limiting the record of rising I/(Ca + Mg) to intervals of sufficient O_2 production and concomitant IO_3^- accumulation. Similarly, post-GOE carbonates lacking iodine (Table 1) may have been deposited under locally anoxic conditions despite a general rise in surface ocean oxygen availability, but without a more comprehensive geological context, diagenesis cannot yet be ruled out. Further work is needed that specifically addresses IO_3^- incorporation into primary dolomite and its retention during dolomitization of primary calcite. However, retention of primary fabrics in Precambrian dolostones compared to fabric destruction in most Phanerozoic dolostones suggests early dolomite formation in equilibrium with seawater, as opposed to late-stage dolomitization replacing primary calcite in reducing pore fluids (Tucker, 1982). Given this, Precambrian dolostones may be well suited to preserve primary seawater trends, analogous to calcites precipitated in Phanerozoic calcite seas (Stanley and Hardie, 1998). Regardless, the observation that I/(Ca + Mg) ratios are all below the detection limit from the carbonates ranging in age from 3.5 Ga, well before most estimates of initial O_2 production and accumulation, to 2.5 Ga (Table 1) is unlikely solely a relic of local diagenetic loss, arguing against appreciable and persistent iodine redox cycling throughout the Archean within the resolution of our data.

Great Oxidation Event

We find the first convincing evidence for an oxidative marine iodine cycle in the ca. 2.45–2.4 Ga carbonates of the Turee Creek Group of the Hardey and Duck Creek synclines in Western Australia. The studied carbonates in the Hardey syncline are located above the glacial diamictite of the Meteorite Bore Member (Krapež, 1996; Bekker et al., 2002). The Meteorite Bore Member is correlated to the Ramsay Lake Formation of the Huronian Supergroup, Canada (Swanner et al., 2013), deposited prior to the permanent loss of NMD-S signal at ca. 2.32 Ga (Bekker et al., 2004). An absence of the Meteorite Bore Member in the Duck Creek syncline makes the age of these rocks less certain relative to glacial events, but these carbonates are inferred to precede deposition of the Meteorite Bore Member (Krapež, 1996). Though the timing and stratigraphic position of the loss of NMD-S signal in the Turee Creek Group is still unconstrained (Swanner et al., 2013), the correlation to other intervals with multiple sulfur isotope data suggests the potential for aerobic iodine cycling prior to the permanent loss of NMD-S signal. The timing of the increase in I/(Ca + Mg) is generally consistent with increasing enrichments in redox-sensitive trace metals such as Mo and Re in Neoarchean organic-rich shales linked to at least transient oxygen accumulation (Anbar et al., 2007). Surface ocean IO_3^- formation prior to the permanent loss of NMD-S signal could be explained with two scenarios: (1) dissolved O_2 in shallow seawater was sufficiently high, at least locally (perhaps in oxygen oases), for IO_3^- accumulation, while atmospheric O_2 was low enough for continued generation and preservation of the NMD-S signal (Pavlov and Kasting, 2002), or (2) both the atmosphere and surface ocean accumulated significant amounts of O_2, but the NMD-S fractionations found in deposits of this age were inherited from earlier atmospheric conditions through crustal recycling of sulfur (Reinhard et al., 2013). Regardless, the I/(Ca + Mg) record indicates surface ocean IO_3^- formation, implying a switch to more oxidizing surface ocean conditions at 2.45–2.4 Ga, broadly coincident with the beginning of the GOE (Lyons et al., 2014).

Resolving the significance of the observed rise in I/(Ca + Mg) during the GOE demands an understanding of modern iodine cycling. The main controls on $[IO_3^-]$ in surface waters are IO_3^- reduction either microbially or photochemically (Küpper et al., 2011), IO_3^- advection from oxic deep waters, and *in-situ* IO_3^- production (Luther et al., 1995). Independent geochemical evidence suggests a redox-stratified ocean before and after the GOE, with sulfidic anoxic conditions prominent along continental margins and Fe-rich anoxic conditions prevailing in the deeper ocean (Planavsky et al., 2011). A redox-stratified ocean would imply a GOE iodine cycle conceptually similar to that in the modern Black Sea where advection of iodine from deep waters is in the form of I^- (Luther and Campbell, 1991; Wong and Brewer, 1977), and with IO_3^- formation and accumulation up to 150 nM (Wong and Brewer, 1977; Luther and Campbell, 1991) via oxidation outpacing photochemical and biotic IO_3^- reduction in the surface waters (Truesdale et al., 2001). Oxidation of I^- to IO_3^- is biologically mediated in the modern ocean (Küpper et al., 2011), and oxidants stronger than O_2, such as O_3 and H_2O_2, are considered to be essential to produce IO_3^- abiotically but cannot account for the abundance of IO_3^- in the modern ocean (Luther et al., 1995). Though the pathways of marine IO_3^- formation are still debated, IO_3^- is exclusively observed in well-oxygenated waters and is completely reduced to I^- with the onset of anoxic conditions (Wong and Brewer, 1977; Emerson et al., 1979; Wong et al., 1985; Luther and Campbell, 1991). These observations point to O_2 accumulation in the surface ocean and related IO_3^- stabilization as the driver for the first increase in I/(Ca + Mg) ratios during the GOE.

We place a tentative threshold for an aerobic iodine cycle in the surface ocean at 1 µM O_2 during the first rise of I/(Ca + Mg) during the GOE. Observations in the oxygen-minimum zone (OMZ) along the eastern coast of the north Pacific Ocean indicate oxygen concentrations ranging from ~225 µM near the ocean surface to as low as 1 µM in the core of the OMZ, with IO_3^- quantitatively reduced in the same interval (Rue et al., 1997). Importantly, these oxygen concentrations are not representative of the levels at which IO_3^- could form but rather the minimum at which we observe IO_3^- accumulation. Given this threshold of O_2 needed to stabilize IO_3^- in marine systems, the apparent absence of a fully oxic and persistent iodine cycle prior to the GOE does not conflict with other recent evidence for local oxidative processes and oxygenic photosynthesis in the Archean, albeit at still low levels. Recent studies have argued for aerobic nitrogen cycling in the surface ocean prior to the GOE (e.g., Thomazo et al., 2011) and local Mn oxidation as early as 3.0 Ga (Crowe et al., 2013; Planavsky et al., 2014), providing early evidence for some surface ocean and even atmospheric O_2 accumulation. The higher reduction potential (pE) for IO_3^-/I^- compared to NO_3^-/N_2 and MnO_2/Mn^{+2} (Rue et al., 1997), the generally lower Gibbs free energy of reaction ($\Delta G_{rxn}°$) for IO_3^- reduction compared to Mn reduction and denitrification (Farrenkopf et al., 1997), and recent observations indicating modern aerobic Mn and N cycling at O_2 concentrations as low as sub-micromolar levels (Clement et al., 2009; Thamdrup et al., 2012) allow for the possibility of aerobic N and Mn cycles in the Archean without widespread IO_3^- or O_2 accumulation. In this light, the shallow Archean ocean might have been functionally anoxic, with its redox state lying between that required for coupled nitrification/denitrification and Mn oxidation and the somewhat higher state required for IO_3^- accumulation. A case consistent with this hypothesis comes from carbonates of the well-preserved 2.7 Ga Tumbiana Formation analyzed in this study, where previous work using nitrogen isotopes has led some workers to infer an aerobic nitrogen cycle (Thomazo et al., 2011), yet iodine concentrations are below detection.

Lomagundi Event

The Lomagundi Event (LE) spans the ca. 2.22–2.1 Ga period and is marked by the largest and longest-lived positive carbonate carbon isotope ($\delta^{13}C_{carb}$) excursion in Earth history, with $\delta^{13}C_{carb}$ rising above +10‰ (Bekker and Holland, 2012). This exceptional $\delta^{13}C_{carb}$ trend has traditionally been interpreted to reflect an increase in relative rates of OM production and burial globally, causing the estimated release of 12–22× the modern atmospheric inventory of O_2 (Karhu and Holland, 1996). Our global record of individual carbonate sections with significant I/(Ca + Mg) ratios deposited during the LE stands in stark contrast to the older data and can be reasonably attributed to a shift to more oxidizing conditions (Table 1; Fig. 1). Other redox proxies, such as marine sulfate evaporites, carbonate-associated sulfate (CAS), and trace metal enrichments recorded in marine sediments, indicate increasing atmospheric and marine oxygenation during the same interval when our evidence points to surface ocean oxygenation (Schröder et al., 2008; Planavsky et al., 2012; Partin et al., 2013).

Starting during the LE, another potential control on I/(Ca + Mg) ratios is the size of the marine iodine reservoir during enhanced OM burial. For example, relatively low I/(Ca + Mg) ratios from carbonate successions deposited during Oceanic Anoxic Events (OAEs), in association with positive $\delta^{13}C_{carb}$ excursions, are interpreted to be the result of a shrinking marine iodine reservoir during the times of enhanced OM burial—in combination with redox shifts and associated IO_3^- reduction (Lu et al., 2010). The Mcheka Formation shows a negative correlation between $\delta^{13}C$ values and I/(Ca + Mg) ratios during the final stage of the LE (Fig. 2). Similar to the OAE, increasing I/(Ca + Mg) ratios in tandem with a decrease in $\delta^{13}C_{carb}$ could result from an increasing marine iodine reservoir following the decline in OM burial. There is scatter and even blank values within the profile, suggesting currently unconstrained diagenetic controls. Nevertheless, the retention of CAS concentration in the same samples (Planavsky et al., 2012), which is a proxy extremely susceptible to diagenetic loss (e.g., Gill et al., 2008), and a lack of correlation between I/(Ca + Mg) and Mg/Ca ratios (Fig. DR1 in the GSA Data Repository[1]) suggest that the overall elevated shift in I/(Ca + Mg) ratios is primary.

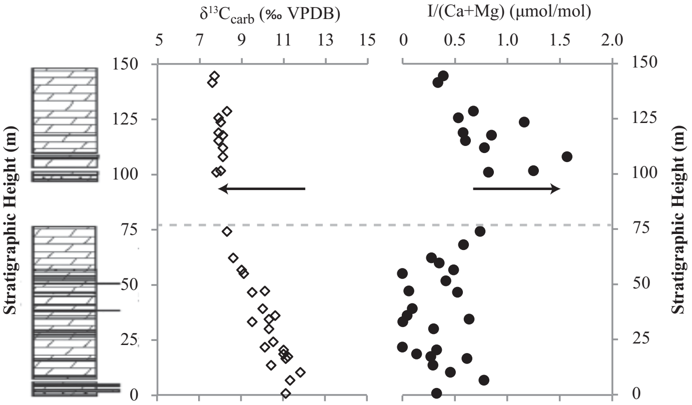

Figure 2. $\delta^{13}C_{carb}$ values from Planavsky et al. (2012) and I/(Ca + Mg) ratios from this study for Mcheka Formation of Zimbabwe (see Table DR2 [see footnote 1]). Note apparent shift (delineated by arrows) to generally higher I/(Ca + Mg) ratios coincident with falling limb of Lomagundi Event. See text for further details. VPDB—Vienna Peedee belemnite.

CONCLUSION

Our results suggest the onset of an oxidative surface ocean iodine cycle during the GOE. Prior to this, redox gradients may have existed in the Archean that allowed for trace and/or transient oxygen levels to support aerobic N and Mn cycles, but the present data suggest an environment dominantly hostile to IO_3^- accumulation and thus one that was mostly anoxic. During the Lomagundi excursion, a general increase in carbonate units with nonzero I/(Ca + Mg) ratios implies widespread IO_3^- stability in the surface ocean related to O_2 concentrations above 1 µM. Although large spatiotemporal gaps still exist for the I/(Ca + Mg) record, our results provide a proof of concept, highlighting the proxy's promise even in very old carbonate rocks with varying degrees of alteration. The importance of this approach is elevated significantly by its relevance to shallow, carbonate-dominated settings, which are not well suited to interrogation by most other paleoredox proxies.

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[1] GSA Data Repository item 2014228, age references, data, and additional information regarding Turee Creek and Mcheka carbonates, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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REFERENCES CITED

Anbar, A.D., et al., 2007, A whiff of oxygen before the Great Oxidation Event?: Science, v. 317, p. 1903–1906, doi:10.1126/science.1140325.

Bekker, A., and Holland, H.D., 2012, Oxygen overshoot and recovery during the early Paleoproterozoic: Earth and Planetary Science Letters, v. 317, p. 295–304, doi:10.1016/j.epsl.2011.12.012.

Bekker, A., Krapež, B., and Karhu, J.A., 2002, Preliminary chemostratigraphic data on carbonates from the Paleoproterozoic Turee Creek Supersequence and Wooly Dolomite of Western Australia: 16th International Sedimentologic Congress, Abstract Volume, p. 26–27.

Bekker, A., Holland, H.D., Wang, P.L., Rumble, D., III, Stein, H.J., Hannah, J.L., Coetzee, L.L., and Beukes, N.J., 2004, Dating the rise of atmospheric oxygen: Nature, v. 427, p. 117–120, doi:10.1038/nature02260.

Broecker, W.S., Peng, T.H., and Beng, Z., 1982, Tracers in the Sea: New York, Lamont-Doherty Geological Observatory, Columbia University, 690 p.

Clement, B.G., Luther, G.W., and Tebo, B.M., 2009, Rapid, oxygen-dependent microbial Mn(II) oxidation kinetics at sub-micromolar oxygen concentrations in the Black Sea suboxic zone: Geochimica et Cosmochimica Acta, v. 73, p. 1878–1889, doi:10.1016/j.gca.2008.12.023.

Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R., and Canfield, D.E., 2013, Atmospheric oxygenation three billion years ago: Nature, v. 501, p. 535–538, doi:10.1038/nature12426.

Emerson, S., Cranston, R.E., and Liss, P.S., 1979, Redox species in a reducing fjord: Equilibrium and kinetic considerations: Deep-Sea Research, v. 26, p. 859–878, doi:10.1016/0198-0149(79)90101-8.

Farrenkopf, A.M., Luther, G.W., III, Truesdale, V.W., and Vander Weijden, C.H., 1997, Sub-surface iodide maxima: Evidence for biologically catalyzed redox cycling in Arabian Sea OMZ during the SW intermonsoon: Deep-Sea Research, Part II: Topical Studies in Oceanography, v. 44, p. 1391–1409, doi:10.1016/S0967-0645(97)00013-1.

Gill, B.C., Lyons, T.W., and Frank, T.D., 2008, Behavior of carbonate-associated sulfate during meteoric diagenesis and implications for the sulfur isotope paleoproxy: Geochimica et Cosmochimica Acta, v. 72, p. 4699–4711, doi:10.1016/j.gca.2008.07.001.

Karhu, J.A., and Holland, H.D., 1996, Carbon isotopes and the rise of atmospheric oxygen: Geology, v. 24, p. 867–870, doi:10.1130/0091-7613(1996)024<0867:CIATRO>2.3.CO;2.

Krapež, B., 1996, Sequence stratigraphic concepts applied to the identification of basin-filling rhythms in Precambrian successions: Australian Journal of Earth Sciences, v. 43, p. 355–380, doi:10.1080/08120099608728260.

Küpper, F.C., et al., 2011, Commemorating two centuries of iodine research: An interdisciplinary overview of current research: Angewandte Chemie, v. 50, p. 11,598–11,620, doi:10.1002/anie.201100028.

Loope, G.R., Kump, L.R., and Arthur, M.A., 2013, Shallow water redox conditions from the Permian–Triassic boundary microbialite: The rare earth element and iodine geochemistry of carbonates from Turkey and South China: Chemical Geology, v. 351, p. 195–208, doi:10.1016/j.chemgeo.2013.05.014.

Lu, Z., Jenkyns, H.C., and Rickaby, R.E.M., 2010, Iodine to calcium ratios in marine carbonates as a paleo-redox proxy during oceanic anoxic events: Geology, v. 38, p. 1107–1110, doi:10.1130/G31145.1.

Luther, G.W., III, and Campbell, T., 1991, Iodine speciation in the water column of the Black Sea: Deep-Sea Research, Part I: Oceanographic Research Papers, v. 38, p. S875–S882, doi:10.1016/S0198-0149(10)80014-7.

Luther, G.W., III, Wu, J., and Cullen, J.B., 1995, Redox chemistry of iodine in seawater revisited: Frontier molecular orbital theory considerations: Advances in Chemistry Series, v. 244, p. 135–155, doi:10.1021/ba-1995-0244.ch006.

Lyons, T.W., Reinhard, C.T., and Planavsky, N.J., 2014, The rise of oxygen in Earth's early ocean and atmosphere: Nature, v. 506, p. 307–315, doi:10.1038/nature13068.

Muramatsu, Y., and Wedepohl, K.H., 1998, The distribution of iodine in the Earth's crust: Chemical Geology, v. 147, p. 201–216, doi:10.1016/S0009-2541(98)00013-8.

Partin, C.A., Lalonde, S.V., Planavsky, N.J., Bekker, A., Rouxel, O.J., Lyons, T.W., and Konhauser, K.O., 2013, Uranium in iron formations and the rise of atmospheric oxygen: Chemical Geology, v. 362, p. 82–90, doi:10.1016/j.chemgeo.2013.09.005.

Pavlov, A.A., and Kasting, J.F., 2002, Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic Archean atmosphere: Astrobiology, v. 2, p. 27–41, doi:10.1089/15311070275362132l.

Planavsky, N.J., McGoldrick, P., Scott, C.T., Li, C., Reinhard, C.T., Kelly, A.E., Chu, X., Bekker, A., Love, G., and Lyons, T.W., 2011, Widespread iron-rich conditions in the mid-Proterozoic ocean: Nature, v. 477, p. 448–451, doi:10.1038/nature10327.

Planavsky, N.J., Bekker, A., Hofmann, A., Owens, J.D., and Lyons, T.W., 2012, Sulfur record of rising and falling marine oxygen and sulfate levels during the Lomagundi event: Proceedings of the National Academy of Sciences of the United States of America, v. 109, p. 18,300–18,305, doi:10.1073/pnas.1120387109.

Planavsky, N.J., et al., 2014, Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event: Nature Geoscience, v. 7, p. 283–286, doi:10.1038/ngeo2122.

Reinhard, C.T., Planavsky, N.J., and Lyons, T.W., 2013, Long-term recycling of rare sulphur isotope anomalies: Nature, v. 497, p. 100–103, doi:10.1038/nature12021.

Rue, E.L., Smith, G.J., Cutter, G.A., and Bruland, K.W., 1997, The response of trace element redox couples to suboxic conditions in the water column: Deep-Sea Research, v. 44, p. 113–134, doi:10.1016/S0967-0637(96)00088-X.

Schröder, S., Bekker, A., Beukes, N.J., Strauss, H., and Van Niekerk, H.S., 2008, Rise in seawater sulphate concentration associated with the Paleoproterozoic positive carbon isotope excursion: Evidence from sulphate evaporites in the ~2.2–2.1 Gyr shallow-marine Lucknow Formation, South Africa: Terra Nova, v. 20, p. 108–117, doi:10.1111/j.1365-3121.2008.00795.x.

Sharp, Z.D., and Draper, D.S., 2013, The chlorine abundance of Earth: Implications for a habitable planet: Earth and Planetary Science Letters, v. 369, p. 71–77, doi:10.1016/j.epsl.2013.03.005.

Stanley, S.M., and Hardie, L.A., 1998, Secular oscillations in the carbonate mineralogy of reef building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 144, p. 3–19, doi:10.1016/S0031-0182(98)00109-6.

Swanner, E.D., Bekker, A., Pecoits, E., Konhauser, K.O., Cates, N.L., and Mojzsis, S.J., 2013, Geochemistry of pyrite from diamictites of the Boolgeeda Iron Formation, Western Australia, with implications for the GOE and Paleoproterozoic ice ages: Chemical Geology, v. 362, p. 131–142, doi:10.1016/j.chemgeo.2013.07.022.

Thamdrup, B., Dalsgaard, T., and Revsbech, N.P., 2012, Widespread functional anoxia in the oxygen minimum zone of the Eastern South Pacific: Deep-Sea Research, Part I: Oceanographic Research Papers, v. 65, p. 36–45, doi:10.1016/j.dsr.2012.03.001.

Thomazo, C., Ader, M., and Philippot, P., 2011, Extreme ^{15}N-enrichments in 2.72-Gyr-old sediments: Evidence for a turning point in the nitrogen cycle: Geobiology, v. 9, p. 107–120, doi:10.1111/j.1472-4669.2011.00271.x.

Truesdale, V.W., Watts, S.F., and Rendell, A.R., 2001, On the possibility of iodide oxidation in the near surface of the Black Sea and its implications to iodine in the general ocean: Deep-Sea Research, Part I: Oceanographic Research Papers, v. 48, p. 2397–2412, doi:10.1016/S0967-0637(01)00021-8.

Tucker, M.E., 1982, Precambrian dolomites: Petrographic and isotopic evidence that they differ from Phanerozoic dolomites: Geology, v. 10, p. 7–12, doi:10.1130/0091-7613(1982)10<7:PDPAIE>2.0.CO;2.

Wong, G.T.F., and Brewer, P.G., 1977, Marine chemistry of iodine in anoxic basins: Geochimica et Cosmochimica Acta, v. 41, p. 151–159, doi:10.1016/0016-7037(77)90195-8.

Wong, G.T.F., Takayanagi, K., and Todd, J.F., 1985, Dissolved iodine in waters overlying and in the Orca Basin, Gulf of Mexico: Marine Chemistry, v. 17, p. 177–183, doi:10.1016/0304-4203(85)90072-6.

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An iodine record of Paleoproterozoic surface ocean oxygenation

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