IRISH RESEARCH COUNCIL
An Chomhairle um Thaighde in Éirinn

TRINITY COLLEGE DUBLIN
COLÁISTE NA TRÍONÓIDE
THE UNIVERSITY OF DUBLIN

Oxygenation Symposium

Trinity College Dublin, Department of Geology

(Museum Building, room M4)

10th & 11th September 2014

Wednesday 10th September

09:30-10:00 Registration (Museum Building foyer).

10:00-10:15 Welcome and introduction to the symposium.

10:15-11:00 Regulation of air in the Archaean. Euan G. Nisbet (Royal Holloway, University of London).

11:00-11:20 The Neoarchaean sulphur cycle: new solutions to the non-zero intercept Δ33S–δ34S data arrays and the apparent sulphate mass imbalance. Meabh Gallagher (Trinity College Dublin), Martin J. Whitehouse (Swedish Museum of Natural History), Balz S. Kamber (Trinity College Dublin).

11:20-12:00 Tea / Coffee

12:00-13:00 The MIF-S signature of Archean and Paleoproterozoic oceanic sulfate – implications for oxygen. James Farquhar (University of Maryland).

13:00-14:00 Lunch (provided for speakers).

14:00-15:00 Atmospheric oxygenation: towards a unifying model. Quentin Crowley (Trinity College Dublin).

15:00-16:00 Molecular palaeobiology of Precambrian prokaryotes and the evolution of multicellularity. Betty Schirrmeister, Philip Donoghue (University of Bristol).

16:00-16:30 Tea / Coffee.

16:30-17:30 Discussion.

18:00 Evening Meal (provided for speakers).

Oxygenation Symposium

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Thursday 11th September

09:30-10:30 When, why, and how of the Great Oxidation Event. Andrey Bekker (University of California, Riverside).

10:30-11:30 The post-GOE open marine carbon cycle from the late Paleoproterozoic Belcher Group. Dominic Papineau (London Centre for Nanotechnology & University College London) .

11:30-12:00 Tea / Coffee.

12:00-13:00 Paleoredox indicators in the ca. 1.85 Ga Flin Flon paleosol, Mike Babechuk, Balz S. Kamber (Trinity College Dublin). Ronny Schoenberg (University of Tübingen).

13:00-14:00 Lunch (provided for speakers).

14:00-15:00 Terrestrial microbes and the atmosphere of Snowball Earth. Ian Fairchild (University of Birmingham) & Huiming Bao (Louisiana State University).

15:00-16:00 Discussion.

16:00-16:30 Tea / Coffee.

16:30-17:30 Discussion & Concluding Remarks (speakers only).

The Regulation of the Air in the Archaean

Euan G. Nisbet

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Abstract: Perhaps the greatest puzzle of Archaean geology is the sustained habitability of the planet, despite a warming Sun. In particular, the atmosphere, despite its insignificant mass, very disproportionately controls surface temperature and redox setting: hence much of the internal evolution of the planet can be constrained by its outer veil. But the redox balances of the air/ocean system, and the greenhouse temperature, are determined biologically. Life has thus meddled deeply with the thermostat and geochemical equilibria. In particular, the emergence of consortia of methanogenic archaea and sulphate-reducing bacteria may have occurred in early Archaean, and then stabilised and moderated the apparently stable warmth of the mid-Archaean. The virtual absence of sedimentary carbonate, except perhaps in highly alkaline settings, until ~2.9 Ga ago suggests that CO_2 drawdown by oxygenesis began then. Since the late Archaean, the CO_2:O_2 ratio, and hence ocean/atmosphere temperature and pH, may have been determined not by the long-term slow geochemical balances, but by the very immediate and high-flux CO_2-concentrating-mechanism that controls uptake into cyanobacterial carboxysomes. The past is the sum of the presents: each immediate moment must be clement, and the geochemical fluxes of short-term processes dwarf long-term cycles.

The Neoarchaean sulphur cycle: new solutions to the non-zero intercept $\Delta^{33}S$ – $\delta^{34}S$ data arrays and the apparent sulphate mass imbalance

Meabh Gallagher [1]*, Martin J. Whitehouse[2], Balz S. Kamber[1]

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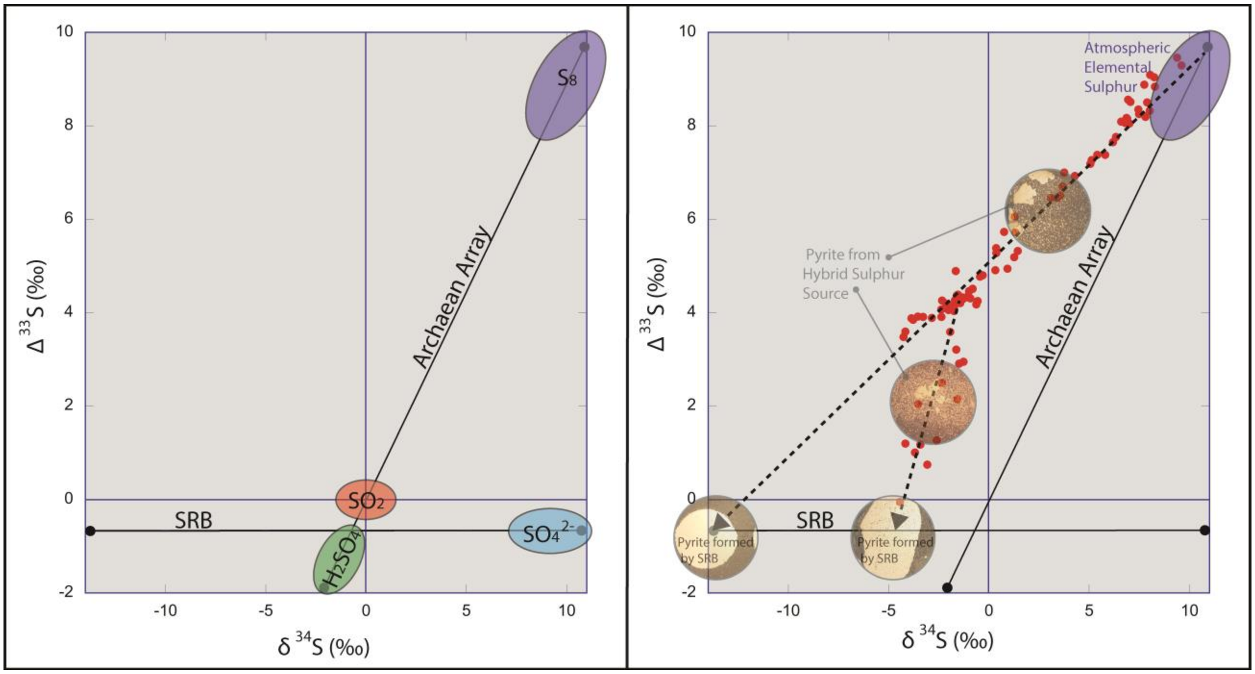
Abstract: We report *in situ* secondary ion mass spectrometer sulphur isotope data for sedimentary pyrite from the 2.52 Ga Upper Campbellrand Subgroup, Transvaal, South Africa. The analysed rock is a shaly limestone from the Gamohaan Formation interpreted to have been deposited in a water depth of ca. 50-100 m. Data were obtained directly from thin section in order to preserve petrographic context. A previous study had discovered that on the 3-isotope plot the pyrites define a linear array that does not pass through the origin. Instead the array shows a large offset from the origin towards lighter S, intersecting $\delta^{34}S$ of 0 at $\Delta^{33}S$ of +5, indicating a possible origin from mixing sulphate reducing bacteria (SRB)-mediated sulphate with atmospheric S_8. The present study revisited the sample, carrying our further analyses of this $\delta^{34}S$ depleted pyrite. The new data confirm and expand the previous observation of a mixing array. A combination of recycled S from sulphides that had originally formed by SRB with elemental S thus explains isotope compositions of sulphides plotting to the left of the atmospheric array at a $\Delta^{33}S$ value intermediate between H_2SO_4 and S_8. It is curious that many Neoarchaean pyrites of likely sulphate origin do not plot at more negative $\Delta^{33}S$, particularly since the positive $\Delta^{33}S$ pool was very extreme. In the case of the studied sample, it appears that the full extent $\delta^{34}S$ and $\Delta^{33}S$ of sulphate is not recorded because S was locally cycled and the true isotopic spread was telescoped into a narrower array. Alternatively, S that entered the Neoarchaean atmosphere did not have an average composition of CD troilite but had become, on average, positive in $\Delta^{33}S$, possibly due to preferential recycling of black-shale hosted pyrite in subduction zones.



Graphic abstract: The Neoarchaean sulphur cycle: new solutions to the non-zero intercept Δ33S – δ34S data arrays and the apparent sulphate mass imbalance (Meabh Gallagher, Martin J. Whitehouse, Balz S. Kamber).

The MIF-S signature of Archean and Paleoproterozoic oceanic sulfate – implications for oxygen

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Abstract: Mass independent sulfur isotope signatures (MIF-S) are observed in a wide variety of rock types and are considered to be a continuous tracer of oxygen levels, possibly even providing a way to capture the rise of oxygen. The preservation of MIF-S in the rock record is, however, subject to processes that may complicate the interpretation of the record of atmospheric oxygen. It has been argued that oxidation reactions may mobilize preexisting MIF-S signatures, potentially generating false signatures for low oxygen even after oxygen levels rose. It has also been recognized that other oxygen 'threshold' sensors may record evidence of low level oxygenation that was too low to shut off MIF-S, but that may have driven oxidation of sulfides to sulfate, providing another source of MIF-S to the oceanic sulfate pool. In both of these cases, the concentration and isotopic composition of oceanic sulfate has the potential carry key information about oxidation and in turn about oxygen levels. The context for this is provided by inferences about atmospheric exit channels for sulfate which are inferred to carry negative $\Delta^{33}S$, and also because some barites, biogenic pyrite, and VMS sulfides have negative $\Delta^{33}S$. This context has led to the assertion that oceanic sulfate had negative $\Delta^{33}S$ throughout the Archean. It is not clear when (or even whether) the signature of negative $\Delta^{33}S$ was masked by a signature of oxidation, but it is thought that evidence may exist for this possibility. My presentation will focus on the nature of the MIF-S signature of oceanic sulfate, describing evidence for negative $\Delta^{33}S$ as well as possible for positive $\Delta^{33}S$. It will also explore whether evidence exists for either or both of the cases for oxidative weathering described above.

Atmospheric oxygenation: towards a unifying model

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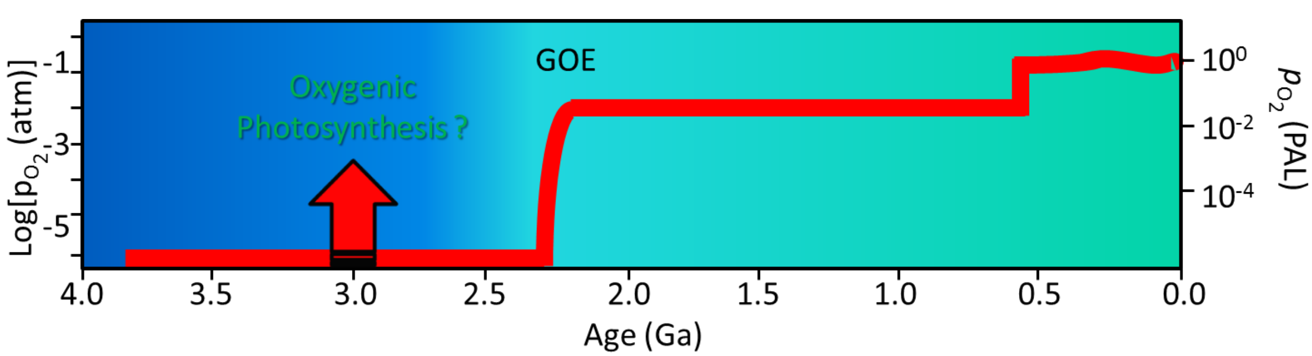
Abstract: It is widely believed that atmospheric oxygen saturation rose from $<10^{-5}$ present atmospheric level (PAL) in the Archean to $>10^{-2}$ PAL at the Great Oxidation Event (GOE) at ca. 2.4 Ga, but it is unclear if any earlier oxygenation events occurred. Recent studies of paleosols from eastern India (Keonjhar Paleosol, Singhbhum Craton) and South Africa (Nsuze Paleosol, Kaapvaal Craton) have provided chemical evidence for transient Mesoarchean atmospheric oxygenation events at ca. 3.02 and 2.96 Ga respectively. These paleosols are considered to preserve the earliest known terrestrial evidence for oxygen accumulation in the Earth's atmosphere, with far-reaching implications from both atmospheric and biological evolutionary perspectives. Chemical signatures from these Mesoarchean paleosols are thought to signify the presence of molecular oxygen at levels higher than those attributable to photo-dissociation of atmospheric water alone. Such elevated levels of atmospheric oxygen could only be due to the presence of a sufficiently large biomass of micro-organisms capable of oxidative photosynthesis. Although considerably earlier than most estimates, according to molecular phylogeny the development of oxidative photosynthesis as a metabolic process in Mesoarchean times appears to be feasible. Archean paleosols which pre- and post-date ca. 3.0 Ga, however do not show any evidence for oxidation and appear to contradict the notion of an early surface oxygenation event. Furthermore, the marine rock record demonstrates that ocean waters only became widely oxygenated during the GOE and this coincided with a major change in ocean chemistry. Some recent studies however, have presented isotope evidence for Mesoarchean oxygenation of near-shore and shallow marine environments. With an unprecedented number of datasets from the Archean and Paleoproterozoic now available, it may now be possible to integrate several apparently contradictory lines of geological and geochemical evidence to present a viable and unifying model for oxygenation of the Earth's atmosphere and oceans.



Molecular palaeobiology of Precambrian prokaryotes and the evolution of multicellularity

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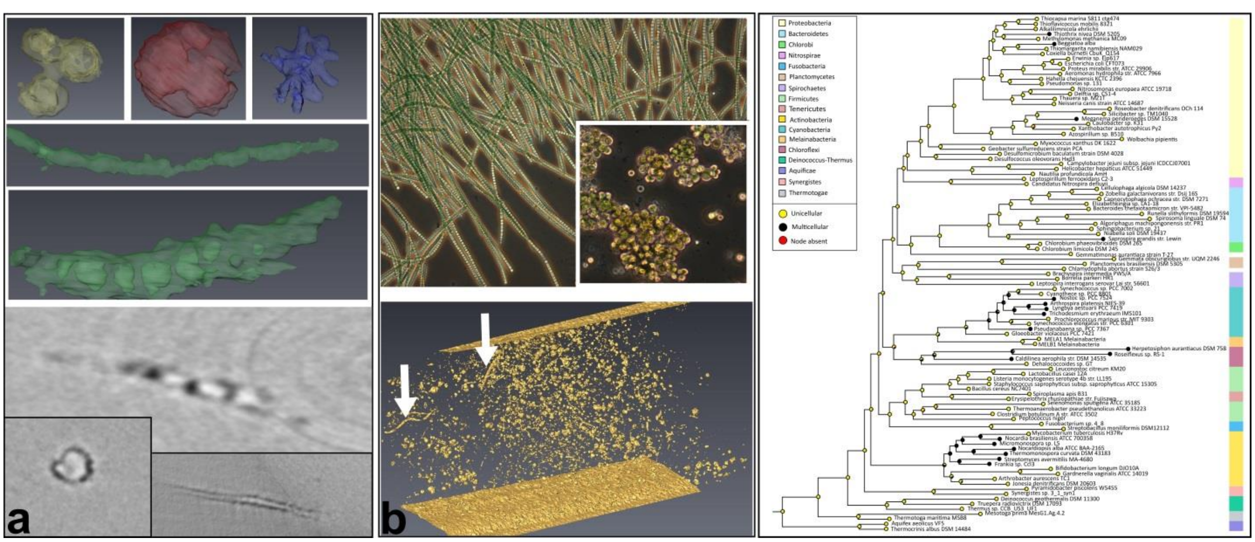
Abstract Life originated more than 3.45 billion years ago. Throughout the Precambrian, prokaryotes are the dominant form of life on Earth. They are responsible for major environmental changes like the rise of oxygen in Earth's atmosphere more than 2.4 billion years ago, known as the Great Oxidation Event (GOE). Although, the early existence of life is widely acknowledged, uncertainties for many Precambrian fossils remain regarding their taxonomic identity and biogenicity. To understand the early evolution of life new methods and techniques, such as molecular phlylogenomics and 3D analyses of fossilized material, may help overcome restrains of poor preservation. Novel sequencing techniques have gained impressive amounts of genome data which, combined with phylogenetic tools, such as molecular clocks may increase our understanding of the evolutionary history of lineages with little or no fossil record. However, although, molecular methods are promising, researchers should be aware that results can depend strongly on models and fossils used in the analyses and close collaborations between palaeontologists and molecular biologists are of immense importance. We have reconstructed phylogenomic trees and estimated divergence times using various Maximum Likelihood and Bayesian methods. Results suggest an origin of cyanobacteria in the Archean Eon and an association of the origin of cyanobacterial multicellularity with the rise of oxygen 2.4 billion years ago. Additionally, 3D reconstructions of fossil assemblages applying Synchrotron Radiation X-ray Tomographic Microscopy support an early diversification of prokaryotes shortly after the GOE and provide novel lines of evidence to better understand the origin and early evolution multicellularity in prokaryotes.



3D reconstructions microfossils and the evolution of multicellularity among prokaryotes

When, why, and how of the Great Oxidation Event

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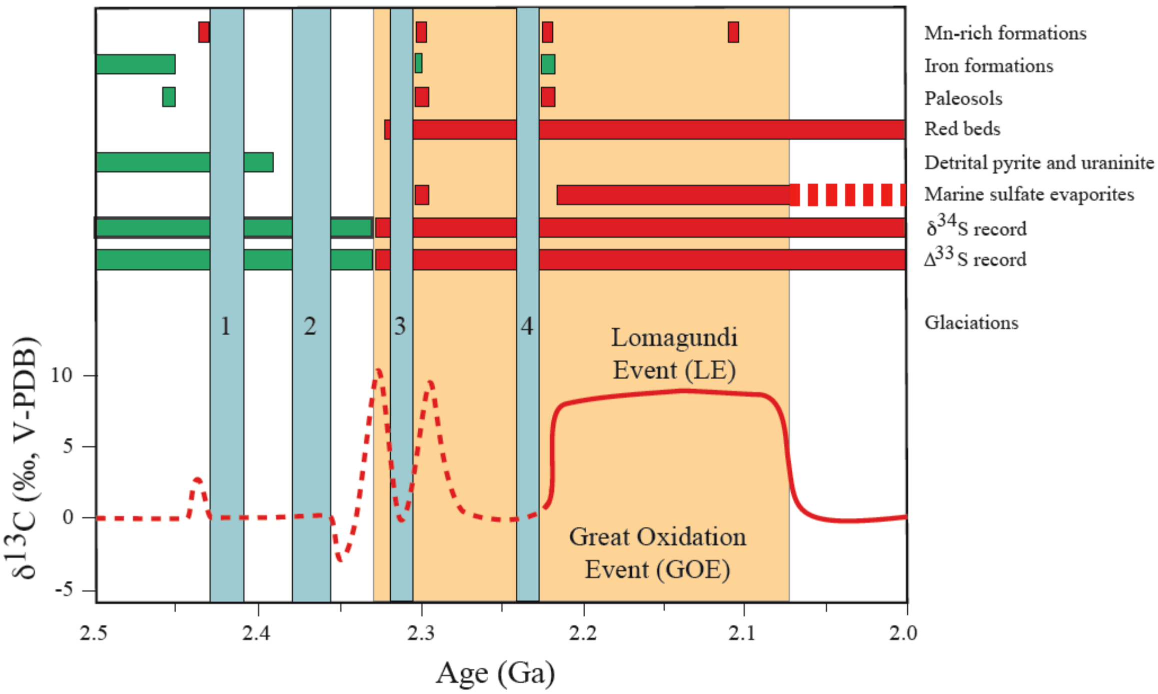
Abstract: Transition from the Archean, largely anoxic atmosphere and ocean to the Proterozoic oxidizing surface conditions has been inferred from geochemical and geological evidence as early as 1927 in Zimbabwe. Subsequent studies provided additional support for this interpretation, bracketed the transition between 2.45 and 2.32 Ga, and suggested temporal and cause-and-effect relationship with a series of the early Paleoproterozoic ice ages (including 4 discrete events). Recently recognized transient oxidation events of the Archean add texture to this pattern, but do not change it. The rise of atmospheric oxygen requires a misbalance between oxygen sinks and sources and most attention was focused on sinks. In contrast, change in oxygen supply related to low organic productivity in Archean oceans with limited nutrient contents are considered here. Although carbon isotope values of carbonates and organic carbon indicate substantial relative burial rate of organic carbon during the Archean, most of the earlier buried organic matter was recycled to sediments at that time during continental weathering, implying very low productivity and burial of 'new' organic carbon. Low contents of redox-sensitive elements, such as Mo, Cu, Zn, and V, in Archean seawater could have kept organic productivity and oxygen production at low levels. The GOE was immediately preceded by deposition of giant iron formations, accounting for more than 70% of world iron resources, and worldwide emplacement of a number of LIPs between 2.5 and 2.45 Ga, indicating enhanced delivery of nutrients and redox-sensitive elements to the oceans via submarine hydrothermal processes and continental weathering under CO_2- and SO_2-rich atmosphere and associated terrestrial acidic runoff. The GOE could have thus been triggered by enhanced nutrient supply to the oceans lifting the limit on biological productivity during a period with intensive mantle plume activity, emphasizing an underappreciated role of endogenic processes as a driver of redox fluctuations in the atmosphere-ocean system.



Graphic abstract: When, why, and how of the Great Oxidation Event (Andrey Bekker). Secular carbon isotope variations in seawater and redox indicators for the oxidation state of the early Paleoproterozoic atmosphere-ocean system (modified from Bekker and Holland, 2012). Four blue vertical bars mark Paleoproterozoic glacial events; the dashed secular carbon isotope curve between 2.5 and 2.22 Ga emphasizes the uncertainty in this part of the curve, the dashed bar for marine sulphate evaporites after ca. 2.07 Ga indicates that sulphate evaporites again became rare in the Paleoproterozoic and Mesoproterozoic record after that time. Deposition of iron formations and Mn-rich deposits indicates anoxic conditions in deep waters. While deposition of iron formations does not necessary require atmospheric oxygen and can be mediated by anoxygenic photosynthetic bacteria, Mn oxidation requires significant levels of atmospheric oxygen.

The post-GOE open marine carbon cycle from the late Paleoproterozoic Belcher Group

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Abstract: The oxygenation of the Paleoproterozoic atmosphere unravelled over several hundred million years between about 2.5 and 2.0 Ga and possibly later. The consequences of atmospheric oxygenation after the 200 million years long $\delta^{13}C_{carb}$ excursion at 2.06 Ga include the common deposition of red beds, increased occurrences of evaporite sulphate, the common presence of carbonate concretions in sedimentary rocks, the increased occurrence of highly ^{13}C-depleted organic matter, the initiation of the first phosphogenic event in Earth history, and the emergence of macroscopic organisms. It is after the end of the $\delta^{13}C_{carb}$ excursion that the Belcher Group of volcano-sedimentary rocks deposited. Because most of Belcher sediments deposited in open-marine conditions, these rocks allow to test some of these observation from elsewhere and to determine the global nature of the unprecedented biogeochemical signals. In the field in the Kasegalik Formation at the bottom of the Group, some stromatolites occur with pink calcite-replaced gypsum crystals and are interbedded with meter-thick red beds. Exceptionally diverse and well-preserved stromatolites (figure 1) occur in the McLeary Formation. Meter-size carbonate concretions in the Tukarak Formation were observed stratigraphically higher and indicate that massive oxidation of organic matter occurred. We also found highly ^{13}C-depleted organic matter, with $\delta^{13}C_{org}$ down to -37.5‰, from black shales and carbonate vents (i.e. white smokers) interbedded in basaltic pillows from the Flaherty Formation. On-going geochemical analyses aim to generate a complete profile of $\delta^{13}C_{carb}$ values for the entire Belcher Group.

Paleoredox indicators in the ca. 1.85 Ga Flin Flon paleosol

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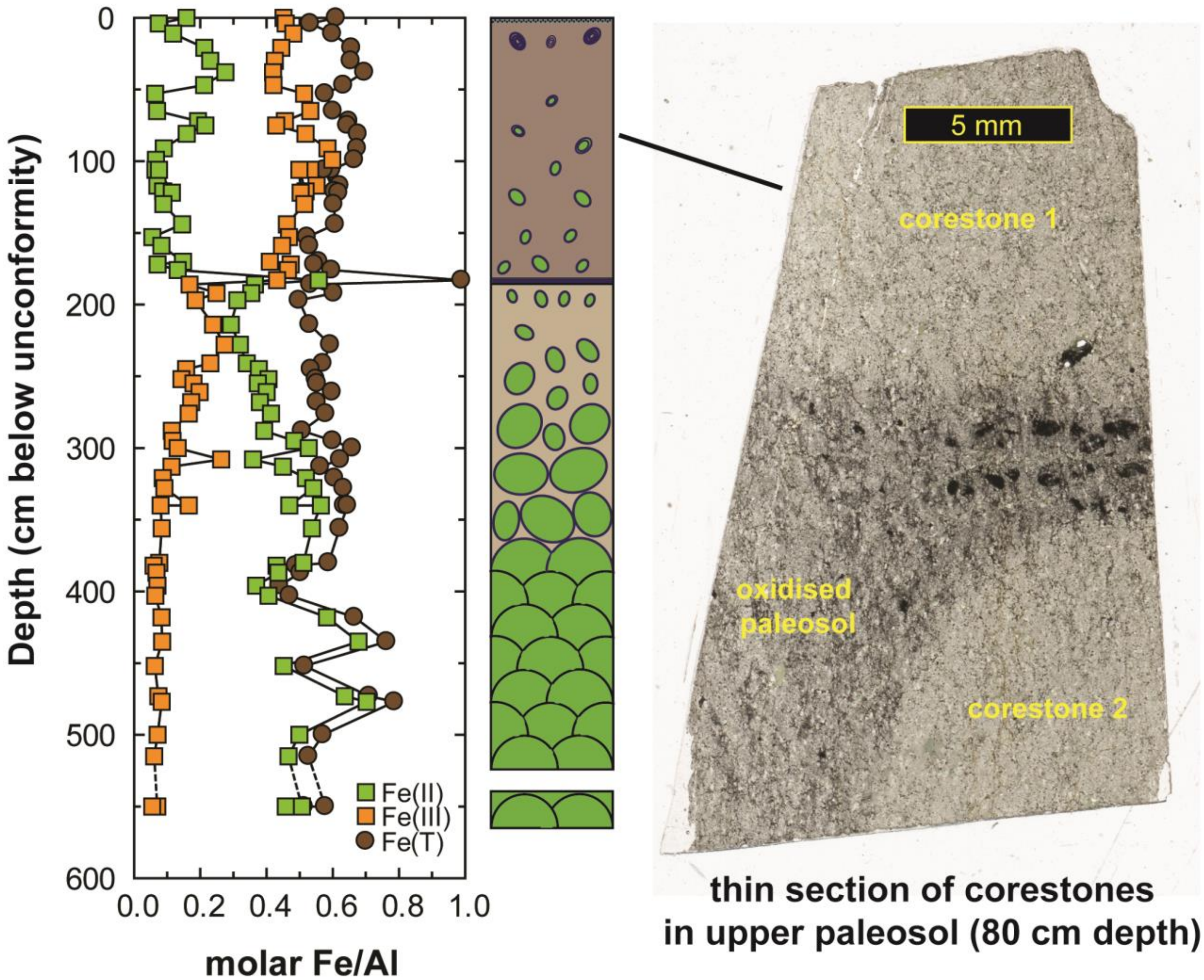
Abstract: A great deal of effort is currently put into 'sniffing' for 'whiffs' of Archean or early Proterozoic atmospheric oxygen. Invariably, these studies employ geochemical proxies that are sensitive to redox conditions. Recent discoveries using these proxies, most notably in Archean paleosols, appear to have pushed back the timing of the onset of oxygenic photosynthesis on Earth to prior to 3.0 Ga by identifying episodic pulses of atmospheric O_2. These new claims contrast with the conventional consensus that the upward loss or redistribution of Fe(II) in all paleosols older than 2.2 Ga was indicative of anoxic or low O_2 weathering conditions. The transition to near-complete Fe(II) oxidation in paleosols younger than 2.2 Ga constitutes some of the strongest evidence for the Great Oxidation Event (GOE).

In this contribution, we revisit a classic post-GOE paleosol with major element, high-precision trace element, and isotopic data to better establish which of the redox-sensitive elements most confidently record an oxidative weathering signature. The paleosol displays the anticipated upward conversion of Fe(II) to Fe(III). By contrast, Mn, which is known to be an element that forms oxides crucial for the further oxidation of other elements [e.g. Cr(III) and Ce(III)], displays a prominent upward depletion that suggests it was lost predominantly as soluble Mn(II). This is a significant observation since Ce anomalies are not well-developed and Cr displays an unusual isotopic signature that is apparently not compatible with Cr(VI) formation. Thus, even though this classic and exceptionally well-preserved paleosol shows Fe(II) oxidation, other redox proxies could erroneously be interpreted as being compatible with anoxic weathering. Sophisticated redox proxies should therefore be applied in combination with characterization of Fe valency and care should be taken to study bona fide paleosols with demonstrable features of physical/chemical weathering.



Graphic abstract: Paleoredox indicators in the ca. 1.85 Ga Flin Flon paleosol (Michael G. Babechuk, Balz S. Kamber, Ronny Schoenberg).

Terrestrial microbes and the atmosphere of Snowball Earth

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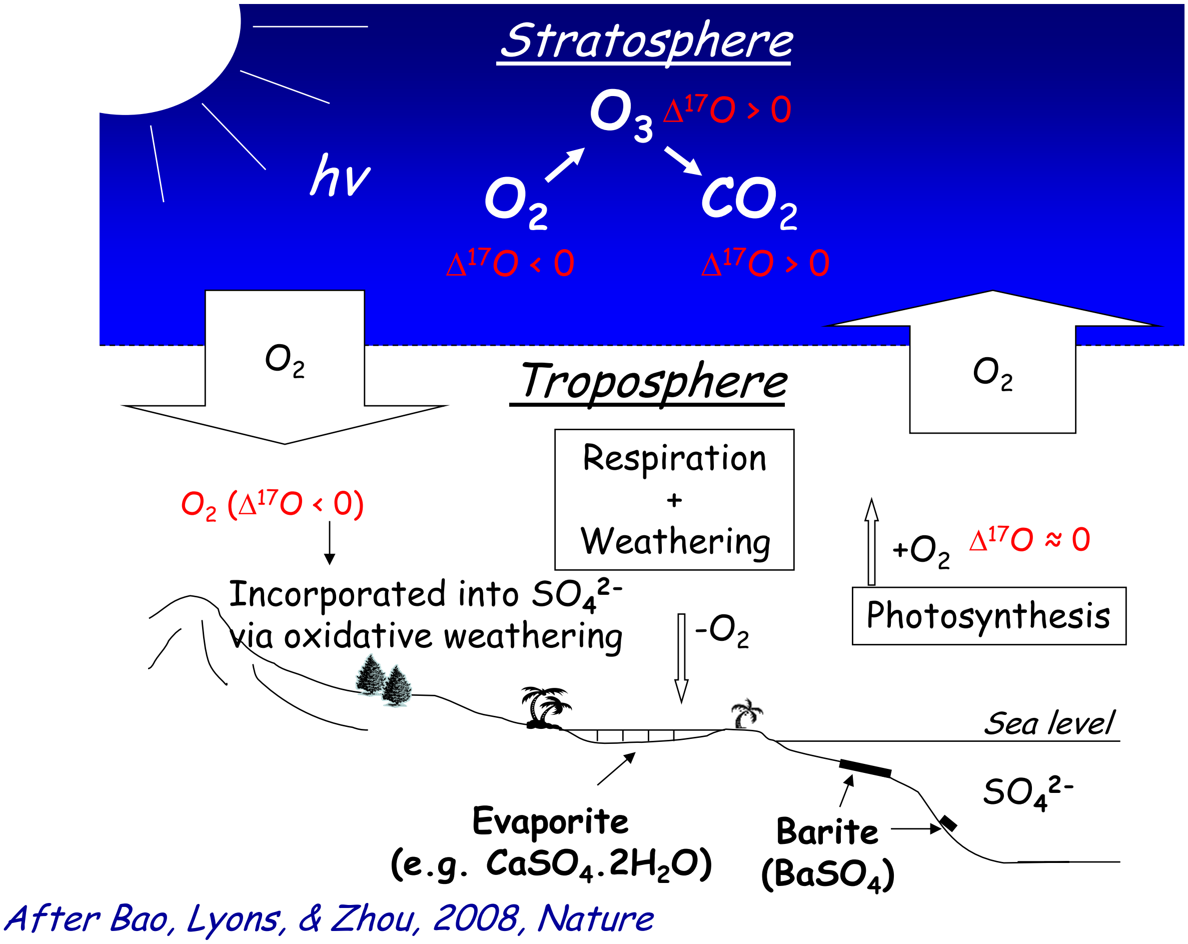
Abstract: Whereas there has been much angst about the habitability of marine environments during a Snowball Earth, little attention has been paid to the continental realm. A unique record of conditions on land is found in the late Cryogenian Wilsonbreen Formation of Svalbard, which is the local expression of the Marinoan panglaciation. Here the 160 m-thick sedimentary record is thought to be entirely non-marine and contains subglacial and waterlain glacial sediment interrupted by intervals of fluvial and lacustrine sediments. These resemble the environments of the modern McMurdo Dry Valleys of Antarctica, although Svalbard was thought to be in the sub-tropics at the time. The Formation was probably deposited over a period of several Milankovitch cycles during the initial phases of meltdown of the ice sheets, but prior to marine flooding. Under such conditions, general circulation modelling supports the idea of extensive ice-free areas on land. In the harsh modern environment, microbial activity dominates and arguably a similar range of organisms would have been present. Macroscopic evidence of microbial activity is provided by stromatolitic limestones (with highly negative $\Delta^{17}O_{SO4}$) and dolomites (with heavy $\delta^{18}O_{SO4\&CO3}$) forming in ephemeral streams and lakes, often with distinct, probably annual laminae. The land surface must have been in contact with atmospheric oxygen carrying large magnitudes of anomalous ^{17}O depletion, ultimately derived from stratospheric reactions in an ultra-high pCO_2 atmosphere generated by accumulation of volcanic CO_2. The preservation of anomalous ^{17}O depletion in carbonate-associated sulphate (CAS) in limestones and the absence of it in the adjacent dolostones suggest an intensive microbial sulfate reduction and sulfide oxidation in shallow, highly evaporative water bodies where the formation of dolostones was also favored. Rapid microbial sulfur redox cycling has resulted in little change in the $\delta^{34}S$ but achieved almost thermodynamic equilibrium with water in the $\delta^{18}O$ of the CAS in dolostone phases. Such microbial sulfur cycling is unusual and a clue to this behavior may be that the unusually high Mn/Fe of the Svalbard carbonates prevented the fixation of HS^- by Fe(II), or that the oligotrophic lakes had facilitated an equal expression of reverse enzymatic processes, resulting in full oxygen exchange between sulphate and water. Either way, the Svalbard record provides us a window into a biological world in a continental interior at the initial phases of the Marinoan meltdown.



Graphic abstract: Terrestrial microbes and the atmosphere of Snowball Earth (Ian J. Fairchild, Huiming Bao).