

EUG XI



Symposium BG02

Oxygen and Evolution

Convenor

Martin Brasier

BG02 Oxygen and Evolution

Sunday PM Session

BG02 : SUPm26 : G1

New Insights into the History of Oxygen Growth

Bruce Runnegar (runnegar@ucla.edu)

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA

Several different lines of geochemical evidence - survival of detrital siderite, pyrite and uraninite; heavy carbonate carbon isotope ratios; the redox state of paleosols; and the end of mass independent sulfur isotope fractionations all point to a major rise in the oxygen content of the atmosphere during the Paleoproterozoic. Comparable geochemical criteria suggest that oxygen levels may have fluctuated widely just before the Cambrian explosion and during the late Paleozoic. Some of these effects may have significantly affected the growth of biospheric complexity, whereas others may have been initiated and driven by biospheric evolution. This is an attempt to reconcile gross features of the fossil record with the geochemical evidence for oxygen growth.

BG02 : SUPm27 : G1

Origin of Organisms that Evolve Oxygen

Euan G. Nisbet (e.nisbet@glrhbc.ac.uk)

Dept. Geology, Royal Holloway, Univ. of London, Egham, Surrey, United Kingdom

Oxygenic photosynthesis may be over 3.5 Ga old. The origins of the various component parts of the process may be of even greater antiquity. The 'bacteriochlorophyll-first' hypothesis is currently receiving support from molecular evidence. If correct, it is possible that anoxygenic photosynthesis and bacteriochlorophyll date back to early thermotaxis around hot vents, which pre-adapted the organism to use infra-red light. The Mn-based oxygen evolving complex may have developed to manage oxidation power (and possibly provide a weapon in toxic warfare between cells) in a biofilm or mat. Rubisco's evolution may have long pre-dated its adaptation for use in cyanobacterial photosynthesis. Perhaps the first cyanobacterium was itself a chimera, assembled by genetic exchange between previously symbiotic purple (PSII) and green S (PSI) bacteria living together near a redox boundary in a hydrothermal setting. Nitrogenase may also have a hydrothermal ancestry for its Mo-Fe protein, perhaps supplying H₂ or managing ammonia. That both rubisco and nitrogenase are 'inefficient' and capable of operating contrary-wise is surprising given the high efficiency that evolution has achieved in many ancient enzymes. Perhaps they are 'Qwerty' enzymes, surviving unchanged by power of monopoly.

BG02 : SUPm28 : G1

Pb-Isotopic Evidence for Pre-3700 Ma Oxygenic Photosynthesis

Minik Rosing (minik@savik.geomus.ku.dk)¹ & **Robert Frei** (robertf@geo.geol.ku.dk)²

¹ Geologisk Museum, Oster Voldgade 5-7, Copenhagen K, DK-1350, Denmark

² Geologisk Institut, Oster Voldgade 10, Copenhagen K, Denmark

Metamorphosed pelagic shale from the >3700 Ma Isua supracrustal belt in West Greenland contains up to 0.5 wt.% graphite with $\delta^{13}\text{C}$ values down to -22.8 ‰ [PDB]. This isotopic signature and the mode of occurrence of the carbon particles suggest that the carbon derived from planktonic organisms that fractionated carbon isotopes by their mode of life. The high concentrations of biogenic reduced carbon and the ¹³C depleted nature of the carbon can best be explained by the activity of phototrophic organisms possibly using the rubisco enzyme for CO₂ fixation.

The Pb isotopic composition of the metasediments indicates high U/Pb and low Th/Pb ratios during the early Archaean, followed by a loss of uranium during a late Archaean metamorphic event. Under reducing conditions uranium and thorium is transported in mineral particles and are not fractionated in the sedimentary environment. A strong fractionation of uranium from thorium during sedimentation suggest that uranium was transported to the sedimentary environment as an oxidised solute, and deposited as a consequence of reaction with reduced organic matter.

The uranium-rich and thorium-poor nature of the sediments thus indicates the existence of strong redox contrasts in the environment in which the shales were deposited.

Based on ribosomal RNA phylogeny, it appears that the development of chlorophyll based phototrophic metabolism and oxygen tolerance was developed in thermophilic bacteria at the level of Chloroflexus, possibly prior to the emergence of the first non-extremophile bacteria. The adaptation to non-extreme environments and the colonization of the open oceans by life may have occurred at the same time as, and possibly depended on, the development of oxygenic photosynthesis. The evidence for high planktonic biomass productivity and the presence of redox contrast in the >3700 Ma ocean may suggest that oxygenic photosynthesis had evolved before 3700 Ma.

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Archaean Cyanobacterial Diversity: More Questions than Answers

Martin Brasier (martinb@earth.ox.ac.uk)

Department of Earth Sciences, Parks Road, Oxford, OX3 1PR, UK

Oxygenic photosynthesis may be very ancient indeed. But just how good is the evidence for it? Molecular evidence from bacterial rRNA sequencing, arguably confirms that cyanobacteria are likely to have evolved after the emergence of hyperthermophile methanogenic archaeobacteria but gives no evidence about timing. Arguments for the establishment of a diverse oxygenic, cyanobacterial microbiota in the early Archaean depend mainly upon three kinds of data: biogeochemistry + biomarkers; stromatolites; and microfossils. Since oxygenic photosynthesis by rubisco results in isotopic discrimination against ¹³C, comparison of $\delta^{13}\text{C}$ ratios in organic matter and marine carbonates can be argued to provide an indirect proxy for its existence in rocks >3.7 Ga. But while such values are in broad agreement with values from modern cyanobacteria, they may also lie within the range of anaerobic methanogens. Biomarker evidence for cyanobacterial metabolism could provide support for oxygenic photosynthesis but there is, as yet, little evidence of this until the late Archaean at 2.7 Ga. Stromatolites have been described from various units in the Archaean but their cyanobacterial origin is hard to prove and even their biogenic origin is often controversial. Many so-called stromatolites of Archaean age could also have been formed abiogenically, for example by the rapid marine precipitation of aragonite or by hydrothermal precipitation of barite and chalcocite quartz. The description and interpretation of morphological remains in the form of microfossils preserved in sedimentary rocks must therefore play a crucial role in underpinning any claims for the early emergence of oxygenic photosynthesis. Relatively few such assemblages have been described to date, of which those from the c. 3.46 Ga old cherts of the Apex Basalt, Warrawoona Group in Western Australia hold a key position. Eleven reported species of microfossils (including cyanobacteria-like forms), were interpreted by Schopf (1993) to occur in water-worn carbonate grains that had been transported a long distance before redeposition in a bedded grainstone conglomerate prior to silicification. Major aspects of the preservation and context of this potentially important evolutionary benchmark have received little critical scrutiny. We have examined and re-imaged the type thin sections of microfossil-bearing type material deposited by Schopf (1993) at the Natural History Museum (NHM) in London, and compared them with samples collected from the same horizon during recent field work. The new study involves Automontage image analysis, SEM with microprobe and EDX, and ToF-SIMS. New views on the nature of these microfossils, and on the rocks in which they occur, will be discussed.

Schopf, JW, *Science*, **260**, 640-646, (1993).

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What can the Fossil Biota from the Early Archaean Rock Record Tell us About Atmospheric Oxygen?

Frances Westall (westall@lpi.usra.edu)¹, **Walsh Maud** (evwals@lsu.edu)², **de Vries Sjoukje** (stdevries@geo.ut.nl)³ & **Nijman Wouter** (wnijman@geo.ut.nl)³

¹ Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058, USA

² Institute for Environmental Sciences, Louisiana State University, Baton Rouge, USA

³ Department of Geology, University of Utrecht, Utrecht, Netherlands

Hydrothermal chert horizons in the Early Archaean volcanic successions of the 3.5-3.3 b.y.-old Barberton and Warrawoona greenstone belts in South Africa and Australia, respectively, contain the fossil remains of microbial mats and the filamentous bacteria which presumably created them (Walsh, 1992), as well as co-existing coccoid and rod-shaped microorganisms (Westall et al. 2000). These microorganisms inhabited a shallow water to intertidal environment largely governed by hydrothermal activity. Silica rich fluids exiting the hydrothermal vents directly silicified the microorganisms living around and on the vents, although barite-, carbonate- and iron-rich fluids also produced intercalated sediments and may have been implicated in fossilisation. The material we have investigated has yielded no evidence for the presence of microfossils indicative of oxygenic conditions, such as cyanobacteria. The filamentous microfossils we have observed are 0.2-2 μm in width and can be >100 μm in length. Given the shallow water to intertidal nature of the mats, it is hypothesised that the mat builders may have been photosynthetic organisms. The morphology of the filamentous microfossils resembles that of modern mat-building microbes which are anoxygenic photosynthesizers, such as purple sulphur bacteria. The coccoid microfossils consist of 1 μm diameter spheres, as well as short, stubby, rod-shaped bacteria 0.6-1 μm in length, whereas the longer rods are >1 μm in width and up to 3.8 μm in length. None of these structures shows the morphological characteristics of oxygenic photosynthesizers, such as cyanobacteria. Can the lack of obvious oxygenic microorganisms be taken to mean that there were no such microbes? Lack of evidence does not necessarily mean lack of existence. Moreover, the individual components of a microbial consortia will not necessarily have an equal chance of being preserved as microfossils, i.e. the microbial record from this period may be selective. However, where clearly identifiable cyanobacterial microfossils are preserved (e.g. in Proterozoic formations), they are more easily recognisable as fossils than the non-cyanophyte population. Indeed, their tough polymeric sheath is invoked as the cause of their better preservation potential. If they had been present in the Early Archaean Warrawoona and Barberton cherts, their preservation potential should have been greater than that of the other microorganisms. From the sedimentological point of view, there is no evidence for surficial oxygenic conditions at the time of deposition of the fossiliferous formations. However, certain hematite/goethite-rich horizons capping shallow water cherts may be the results either of hydrothermal exhalations or could have resulted from local oxidation of a subaerially-exposed, iron-rich sediment.

Walsh MM, *Precambrian Res.*, **54**, 271-293, (1992).

Westall F, de Wit MJ, Dann J, van der Gaast S, de Ronde CEJ & Gerneke D, *Precambrian Res.*, in press, (2000).

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Photosynthesis and Early Evolution of the Earth's Atmosphere: Constraints from the Geological Record

Manfred Schidlowski

(paleo@mpch-mainz.mpg.de)

Max-Planck-Institut fuer Chemie, (Otto-Hahn-Institut), Postfach, 55020 Mainz, Germany

There is no doubt that the release of molecular oxygen as a by-product of photosynthetic carbon fixation by plants and autotrophic microorganisms was the most important single process ever to make its impact on the terrestrial atmosphere. Since current photochemical models predict oxygen levels in the prebiological atmosphere within the range 10⁸ to 10¹⁴ PAL (Present Atmospheric Level), we may reasonably infer that life processes alone must be credited with the oxygenation of terrestrial near-surface environments (inclusive of the atmosphere), with free oxygen resulting from the reduction of CO₂ to the carbohydrate level by

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water in a light-powered reaction ($2\text{H}_2\text{O} + \text{CO}_2 \Rightarrow \text{CH}_4 + \text{O}_2$). Hence, the establishment of photosynthesis as the quantitatively most important biochemical process would provide a crucial temporal constraint for the first appearance of an oxygenated atmosphere.

Various disparate lines of evidence suggest that photosynthetic carbon fixation is an ancient process, operated by microbial photoautotrophs as early as 3.5, if not 3.8 Gyr ago. It is, meanwhile, well established that laminated microbial ecosystems made up of microorganisms capable of photosynthesis and phototactic responses were extant as from at least Warrawoona times (3.4-3.5 Gyr). Reduced (organic) carbon in the form of (partly graphitized) kerogen and related substances is a common constituent of sedimentary rocks since the beginning of the record 3.8 Gyr ago. Accordingly, the release of photosynthetic oxidation equivalents (O_2 in the case of water-splitting photosynthesis, SO_4^{2-} and S in the H_2S -based variants) must have commenced at the same time, i.e. extremely early in the Earth's history. Since other evidence argues for a considerably later onset of oxygenated surface conditions (about 2 Gyr ago), a good case can be made that the build-up of substantial atmospheric oxygen pressures was not primarily linked to the process of photosynthesis as such, but rather to the partitioning of oxygen among the principal geochemical reservoirs. Likely candidates of vigorous oxygen-consuming reactions on the early Earth are (1) the oxidation of reduced gas constituents of the primordial atmosphere, (2) the conversion of the ubiquitous dissolved Fe^{2+} -component of the early oceans into the ferric iron constituents of Precambrian banded iron-formation, and (3) the increased cycling rates of seawater through ancient submarine hydrothermal systems exploiting the buffer capacity of the reduced (basaltic) material of the early oceanic crust. With the retention of free oxygen in the atmosphere ultimately resulting from the failure of thermodynamics to exercise strict control over the redox balance of the atmosphere-ocean-crust system, the storage on the 10^6 yr-scale of varying quantities of O_2 in the Earth's volatile envelope had probably always been a function of the kinetics of the oxygen-consuming processes in the surficial compartment of the geochemical cycle.

BG02 : SUPm34 : G1 Biogenic Methane as the Unified Explanation for Archaean Greenhouse Warming, the Rise of Oxygen, and Palaeoproterozoic Glaciation

David Catling (catling@humbabe.arc.nasa.gov),
Christopher McKay
(mckay@galileo.arc.nasa.gov) &
Zahnle Kevin (kzahnle@mail.arc.nasa.gov)
NASA Ames Research Center, Mail Stop 245-3, Space
Science Division, USA

Oxygenic photosynthesis did not make the rise of oxygen inevitable. Archaean carbon burial fluxes were matched by oxygen losses (e.g., to H_2 , CO , SO_2 and Fe^{2+}) and perhaps even set by them [1]. Reducing power from sedimentary organic carbon can also be returned to the atmosphere in the carbon cycle via diagenetic/metamorphic gases. But there is an outlet for reductant that causes truly irreversible oxidation: space. Indeed, hydrogen escape to space is widely believed to have led to the present highly oxidized states of Mars and Venus. Hydrogen escape has been ignored for Archaean Earth because only water vapor has been considered as the hydrogen source. Water is cold-trapped to a few ppmv in the stratosphere, leading to negligible H escape. However, H escape via methane also adds oxygen to the Atmosphere-Ocean-Sedimentary (AOS) system. Photosynthesis and methanogenesis together produce an overall reaction: $\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2$. When hydrogen is lost to space via methane, oxygen is irreversibly gained. $\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + \text{O}_2 + 4\text{H}(\text{space})$. In today's oxygen-rich atmosphere, methane is limited to 1.7 ppmv by rapid oxidation. But prior to the rise of oxygen at 2.3-2.2 Ga, photochemical models demonstrate methane levels ~3000 ppmv [2,3]. Methane is not cold-trapped and H escape to space via methane photolysis is unavoidable. This would have generated huge, irreversible oxidation, ~ 10^{13} mol O_2 equivalents per year. We propose that time-integrated oxidation due to H escape via methane made the rise of oxygen inevitable. Reduced sinks were irreversibly oxidized in the AOS system and photosynthetic O_2 inevitably rose at a redox titration point.

High methane would also explain Archaean greenhouse warming when the sun was 20-30% less luminous [3]. Paleosols indicate $p\text{CO}_2 < 0.04$ bar at 2.75 Ga [4], insufficient by an order of magnitude to prevent Earth from freezing. In a methane-rich Archaean atmosphere, we

deduce $p\text{CO}_2$ to have been low (<0.1 bar) via negative feedback. CO_2 augmentation to methane-dominated greenhouse warming would have led to rapid removal of CO_2 via silicate weathering. During the oxic transition, methane would oxidize with dramatic loss of greenhouse warming. This is consistent with the global glaciation at 2.4-2.2 Ga that coincides with the rise of O_2 according to Huronian paleosols [5]. Today, 20-40 times more organic carbon is metabolized to methane than gets buried. Thus the deleterious effect of O_2 on methanogenesis during the oxic transition may have enhanced carbon burial. We calculate that Proterozoic $p\text{CO}_2$ must subsequently have stabilized at a higher level (~0.1-0.2 bar) than during the late Archaean: a testable prediction. Because light H preferentially escapes from Earth, our theory is also consistent with tentative evidence that Archaean oceans were deuterium-depleted [6].

Holland, HD, *Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ Press), p.360-364, (1984).
Zahnle, K, *J. Geophys. Res.*, **91**, 2819-2834, (1986).
Pavlov, AA, *J. Geophys. Res.*, **105**, 11981-11990, (2000).
Rye, R, Kuo, PK, & Holland HD, *Nature*, **378**, 603-605, (1995).
Prasad, N & Roscoe, SM, *Catena*, **27**, 105-121, (1996).
Taylor, HP, *J. Geol. Soc. London*, **133**, 509-558, (1977).

BG02 : SUPm35 : G1 Fixed Nitrogen Availability: The key to Understanding the Rise of Atmospheric O_2

Janet Siefert (siefert@stat.rice.edu)¹ &
James Kasting (kasting@mars.essc.psu.edu)²
¹ Dept of Statistics-MS138, P.O. Box 1892,
Houston, Texas, 77251-1892, USA
² Geosciences Dept, PSU, State College, PA, USA

Perhaps the most perplexing problem surrounding the rise of atmospheric O_2 is the apparent large time lag between the origin of photosynthesis and the time when indications of free O_2 appear in the geologic record. The identification of methylhopanes in sediments (Brocks et al., 1999) suggests that cyanobacteria were present in the Archaean ecosystem by 2.7 Ga, if not earlier. Geologic indicators, however, place the rise of O_2 at about 2.1-2.3 Ga (Holland, 1994). Why did it take at least 400 million years for O_2 levels to rise? A possible explanation can be found in the availability of fixed nitrogen. Prior to the origin of biological N fixation, the largest source of fixed N would have been hydrolysis of HCN produced photochemically within the atmosphere (Zahnle, 1986). HCN would have hydrolyzed to give ammonium, NH_4^+ . The sink for ammonium would have been conversion to NH_3 followed by photolysis in the atmosphere. We find that this process could have produced dissolved NH_4^+ concentrations on the order of 10^6 M. This is well below the limit of 10^4 M above which biological N fixation is inhibited (Towe, 1994). Prior to the origin of cyanobacteria, anaerobic prokaryotes learned how to fix nitrogen using the enzyme nitrogenase, so biological N fixation superceded the abiotic mechanism. The invention of O_2 -producing photosynthesis by cyanobacteria would have put most of these anaerobes out of business in the surface ocean. Thus, cyanobacterial productivity would have been extremely limited until cyanobacteria themselves devised some way to both fix nitrogen and produce oxygen. This was not easy for them to do because the nitrogenase enzyme is poisoned by O_2 . We suggest here that it was the shared ability that triggered the global O_2 rise at ~2.3 Ga. Today, cyanobacteria employ at least 3 strategies to protect their nitrogenase from O_2 , i) circadian rhythm, ii) spatial separation within colonies, and iii) heterocysts. We are using molecular evolution methods to try to determine when these strategies first evolved. Our investigations indicate that the most promising data are those genes that control circadian rhythms in cyanobacter, the kaiA/B/C genes. These genes are phylogenetically widespread in the cyanobacteria, in nitrogen fixing and non-nitrogen fixing species. Hence they offer the possibility of reconstructing the phylogenetic history of the invention of protection mechanisms as they evolved in cyanobacteria. We report the phylogenetic history of the kaiC gene and the role that circadian rhythm may have played in the rise of O_2 in the late Archaean.

Brocks JJ, Logan GA, Buick R, & Summons RE, *Science*, **285**, 1033-1036, (1999).
Holland HD, *Early Life on Earth*, 237-244, (1994).
Towe KM, *Early Life on Earth*, 36-47, (1994).
Zahnle KJ, *J Geophys Res*, **91**, 2819-2834, (1986).

BG02 : SUPm36 : G1 Oxygen and Evolution of the Precambrian Iron Banded Formations

Dmitri Yegorov (dyegorov@yahoo.com)
Geological Inst KSC RAS, Fersman str 14, Apatity
Murmansk, Russia

Precambrian Banded Iron Formations (BIF) can be subdivided into two major types: Algoma-type (lenticular deposits closely associated with effusive rocks) and Lake Superior-type (thicker deposits in schists). The Superior-type BIFs all over the world are confined mainly to the Lower Proterozoic rocks; in Europe these are huge deposits in Krivoy Rog and Kursk (2200-2000 Ma; Shcherbak et al., 1990). The Algoma-type BIFs occur mostly near the Archean-Proterozoic boundary. In Europe, the largest deposits of this type are located in the Ukrainian Shield (Novopavlovsk, over 3400 Ma, Kosivtsevskaia formation, Near-Azov region, over 3310 Ma, Kosko-Verkhovtsevskaia BIF, 3175-3150 Ma; Shcherbak et al., 1990), and on the Baltic Shield (Kola BIF, Olenegorsk, 2800-2750 Ma, original data; Kostomuksha, 2800-2760 Ma; Bibikova, 1989).

Most researchers interpret the Algoma-type BIFs to be sedimentary or volcanic-sedimentary formations, however (in contrast to the undoubtedly sedimentary BIFs of the Superior-type) this interpretation is more often than not based on insufficient factual evidence. According to our studies of the Kola BIF and the data on the Kostomuksha (Barabanov, 1985) and a number of Archean BIFs of the Ukrainian Shield (Shcherbak et al., 1990), these deposits were formed by metamorphic-metasomatic transformations of primary high-Fe volcanic rocks in Archean granite-greenstone areas.

Isotopic studies of sulphur (Huttori et al., 1983) and carbon (Melezhik and Fallick, 1996) showed that about 2300 Ma ago there was a sharp increase in the oxygen content in the atmosphere, from only a few percent to the modern level. In our opinion, this very event created the necessary prerequisites for huge (as much as 3 km thick) Superior-type BIFs to originate in the course of sedimentation.

And finally, BIFs ceased to originate about 1800 Ma ago. This is usually taken to be the consequence of oxidation of the deep-ocean waters which, as a result, became depleted in iron (Klein, 1997).

Barabanov VF, *Geokhimiya. Leningrad: Nedra*, 424, (1985).
Bibikova EV, *Uranium-lead geochronology of early stages of the evolution of ancient shields. Moscow: Nauka*, 180, (1989).
Hattori K, Krouse HR & Campbell FA, *Science*, **221**, 549-551, (1983).
Klein C, *Nature*, **385**, 25-26, (1997).
Melezhik VA & Fallick AE, *Terra Nova*, **8**, 141-157, (1996).
Shcherbak NP, Artemenko GV, Bartnitsky EN, Tkachenko MV & Plotkina TA, *Isotope dating of endogenic ore formations. Abstracts of the All-Union Conference. Kiev*, 89-92, (1990).

BG02 : SUPm37 : G1 Planetary Evolution and the Early Carbon Isotope Record; Evidence from Western Australian Basins

John Lindsay (john.lindsay@anu.edu.au)¹ &
Martin Brasier (martin.brasier@earth.ox.ac.uk)²
¹ Research School of Earth Sciences, Australian National
University, Canberra ACT 2611, Australia
² Earth Sciences Department, Parks Road, Oxford OX1
3PR, UK

The Late Archaean to Early Palaeoproterozoic basins of Western Australia rest on the Archaean Pilbara Craton or along the Capricorn Orogen which forms the suture between the Pilbara Craton and the adjoining Yilgarn Craton (Tyler & Thorne, 1990). These basins form a time series which contains a stratigraphic record across the critical time interval between 2.7 and 1.8 Ga when the earth's atmosphere and biosphere were evolving rapidly. Stable isotope data from well preserved shallow marine carbonate rocks preserved in these basins provide an important insight into the evolution of the early atmosphere and the evolution of the biosphere.

In the latest Archaean (c. 2.6 Ga) during a tectonically quiescent interval the secular $\delta \delta^{13}\text{C}_{\text{carb}}$ curve is flat and similar to that seen in the later Palaeoproterozoic basins of northern Australia (<1.8 Ga). As the cratons converge,

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beginning at 2.6 Ga and continuing until at least 1.9 Ga, the $\delta^{13}\text{C}_{\text{carb}}$ curve becomes much more dynamic with significant positive and negative excursions. A major positive excursion at between 2.2 and 2.3 Ga can be correlated with a similar global event recognised in Africa, Europe and North America, the so called Lomagundi Event (Karhu and Holland, 1996). Earlier studies of the overlying Mesoproterozoic Bangemall Basin and of similar basins in northern Australia (Brasier and Lindsay, 1998; Lindsay and Brasier, 2000) suggest that, beginning at 1.8 Ga, the $\delta^{13}\text{C}_{\text{carb}}$ curve again becomes monotonic and remains so for most of the following billion years until the Neoproterozoic. The major positive isotopic excursion, the Lomagundi Event, is documented in the back-arc basins formed as the ocean closed and subduction began

The data imply that sequestration of carbon occurs during ocean closure as organic-rich passive margin sediments containing isotopically light carbon are subducted into the lower crust and mantle. A second stepwise increase in atmospheric oxygen in the Neoproterozoic similarly appears connected with ocean closure as the supercontinent, Rodinia, assembled (Des Marais, 1994). This second event has been associated with the development of multicellular life and the evolutionary "Big Bang" (Knoll and Canfield, 1998). This implies that biospheric evolution is driven by the earth's endogenic energy resources and its long term survival depends upon those energy resources. If this is so it has fundamental implications, not only for life on earth and on other planetary bodies. Small planets have limited endogenic energy resources to drive crust/mantle interaction, that is plate tectonics, and are thus only likely to have supported life early in their history. Once the planet's energy resources are expended the biosphere will enter a prolonged stasis and ultimately face extinction.

Brasier, M.D. & Lindsay, J.F., *Geology*, **26**, 555-558, (1998).
Des Marais, D.J., *Chemical Geology*, **114**, 303-314, (1994).
Karhu, J.A. & Holland, H.D., *Geology*, **24**, 867-870, (1996).
Knoll, A.H. & Canfield, D.E., *Isotopic Paleobiology and Paleocology. The Paleontological Society Papers*, **4**, 212-243, (1998).

Lindsay, J.F. & Brasier, M.D., *Precambrian Research*, **99**, 271-308, (2000).

Tyler, I.M. & Thorne, A.M., *Journal of Structural Geology*, **12**, 685-701, (1990).

BG02 : SUPM38 : G1 Tropical Laterites, Atmospheric O₂ and CO₂ Levels, and Life on Land in the Early Proterozoic

Nic Beukes (njb@na.rau.ac.za),
Jens Gutzmer (jg@na.rau.ac.za) &
Herman Dorland

Department of Geology, RAU, PO Box 524, Auckland Park 2006, South Africa

Laterites, Fe³⁺/Al-rich soils of modern day oxygenated humid warm tropical to subtropical environments with lush vegetation, are preserved over ~250,000 km² along a 2.2 Ga old erosional unconformity in the Hekpoort and Wolhaarkop paleosols below a cover of red beds in the Transvaal Supergroup of Southern Africa. Extensive iron-depleted pallid zones in profiles associated with the Hekpoort paleosol, previously interpreted as indicative of a reducing Early Paleoproterozoic atmosphere, are now recognized as incomplete remnants of this continent-wide lateritic paleoweathering event. This indicates that the Precambrian atmosphere became oxygenated earlier than previously thought and disqualify the crucial paleosol evidence for a sudden rise in oxygen levels at 2.2 Ga ago. The retention of ferric iron in the laterites can only be explained if atmospheric CO₂ concentrations were at least two to six times lower than predicted by theoretical climate models. Iron-depleted pallid zones within the paleosols indicate the influence of organic matter, and hence, abundant life on land across the Kaapvaal Craton in the Early Proterozoic. Furthermore it seems possible that the laterites on the Kaapvaal Craton are time-equivalent to the oxidized Hokolampi and Ville Marie paleosols in Finland and Canada respectively. This new information necessitates revision of models for soil formation in the Precambrian by considering the effects of terrestrial biomass. Taking this into account minimum atmospheric oxygen concentrations of between 0.5% and 15% PAL must have been present at the time of formation of the ~2.75 Ga Mt Roe paleosols in Australia. Such high oxygen concentrations are also required to explain the presence of hematite-rich ferricretes and oolitic ironstones in the Timeball Hill Formation of the Pretoria Group (Transvaal Supergroup), situated stratigraphically below the Wolhaarkop-Hekpoort laterite. The

ironstones, which contain hematite pisolites similar to those of modern laterites are observed in a ~100,000 km² area and are about 2.4 Ga in age.

BG02 : SUPM39 : G1 Mapping out Microbial Communities using Stable Isotopes in the 2.7 Ga Belingwe Belt, Zimbabwe

Nathalie, V. Grassineau (nathalie@gl.rhbc.ac.uk) & Euan, G. Nisbet (nisbet@gl.rhbc.ac.uk)
Department of Geology, Royal Holloway University of London, EGHAM TW20 0EX, United-Kingdom

The 2.7 Ga old Belingwe Greenstone Belt (Zimbabwe) comprises several well-preserved suites of sedimentary and volcano-sedimentary rocks that contain a record of microbial activity. Sulphur, carbon and nitrogen isotopes have been studied on sulphide minerals and kerogens in two sulphur- and carbon-rich sediments, and on stromatolites. The analyses have been carried out using the CF-IRMS technique, allowing a high resolution on a scale fine enough for resolving fingerprints of microbial reactions in sediment where bioturbation was absent.

The $\delta^{34}\text{S}$ values obtained on more than 200 sulphide minerals give a range from -20 to +17 ‰. Such a wide range compared to other rock units in the Archaean, suggest a complex ecology involving sulphate reduction and sulphur oxidation. The heterogeneities in the sulphur isotopic compositions can be more than 3 ‰ on a scale as small as one millimetre, and indicate the presence of primary biogenic variation. The $\delta^{13}\text{C}$ has been measured in the organic carbon and the carbonates. The values obtained for the stromatolites are close to 0 ‰ suggesting a photosynthetic process. The $\delta^{13}\text{C}$ in the organic carbon varies from -44 to -7 ‰. There are distinctively different ecological systems represented within this range. However the values are clustered between -32 and -25 ‰, implying the existence of well established aerobic bacterial activity (using the Calvin-Benson cycle).

These results obtained on the millimetre scale allow modeling of the microbial communities. These include: stromatolites, with evidence of abundant oxygenic photosynthesis; shallow-water sediment in which anoxygenic photosynthesis by S bacteria, as well as methanogenesis and methylothrophy, may have occurred; and deeper water fine sediment, perhaps below wave-base, where life may have been supported by sulphureta.

Monday AM Session

BG02 : MOam02 : G1 Baryte-Rich Sedimentary Fe and Mn Oxide Deposits and the Re-Oxygenation of Neoproterozoic Seawater after "Snowball-Earth"

Michael Bau (mibau@geosc.psu.edu)¹,
Bernd Buehn², Peter Dulski³ &
Hiroshi Ohmoto¹

¹ Penn State Astrobiology Research Center, 510 Deike, University Park, PA 16802, USA

² Inst. f. Geowissenschaften, Universitaet Giessen, Senckenbergstr. 3, D-35390 Giessen, Germany

³ GeoForschungsZentrum Potsdam, Telegrafenberg Haus B, D-14473 Potsdam, Germany

The 'Snowball-Earth' hypothesis suggests that during Neoproterozoic glaciation(s) the ice-covered oceans turned an- or suboxic and sustained high concentrations of dissolved Fe and Mn. Melting of the ice-cap would have re-initiated atmosphere-seawater exchange and, hence, re-oxygenation of the an- or suboxic seawaters, resulting in the formation of stratiform deposits of Fe and Mn oxides in the oceans. We studied the Y and REE distributions in ca. 0.72 Ga old hematite quartzites and 'Mn ores' (previously termed 'iron-formation' and 'manganese-formation', resp.) from Otjosondu, Namibia. They are stratigraphically correlated to the Chuos Formation. The upward mineralization sequence is: 1) clastic quartz arenites, 2) 'Mn ore', 3) hematite quartzites, 4) 'Mn ore', and 5) clastic quartz arenites. Previous studies suggested deposition of the 'Mn ore' in relatively shallow, near-shore waters and formation of the Fe oxides in deeper, off-shore waters. The hematite quartzites show shale-normalized REY patterns (Y inserted between Dy and Ho) with LREE = MREE > HREE, no anomalies in Ce and Eu, but a negative anomaly in Y. Hematite quartzites from the transition into the upper Mn horizon show similar patterns but are characterized by positive Ce anomalies. The 'Mn ore' displays patterns with LREE < MREE > HREE, no Eu anomalies, but positive Ce and negative Y anomalies. Ba (which is hosted by barite) concentrations reach levels as high as 7% and increase with increasing Mn content, Mn/Fe ratio and the magnitude of the positive Ce anomaly. We emphasize that REY distribution and high Ba content are in marked contrast to what is typically seen in early Precambrian iron- and manganese-formations, but in close agreement with Cenozoic to modern hydrothermal Fe-Mn crusts, indicating that the Otjosondu Fe-Mn oxides are in fact Neoproterozoic hydrothermal Fe-Mn crusts. However, a rough approximation based on the Ce anomalies suggests high growth rates between 7 to 70 mm/yr, indicating an elevated Fe and Mn flux. The above characteristics of REY and Ba distributions suggest the presence of sulphate-poor anoxic deep waters that were rich in Fe, Mn, Ba and REY due to the predominance of benthic fluxes of these elements. There is no evidence for significant REY input from seafloor basalts via hydrothermal fluids or from oxic continental environments via river water and/or oxic surface water. The depositional sequence of Fe oxides without Ce anomaly, Fe oxides with positive Ce anomaly and finally barite-rich Fe-Mn oxides with positive Ce anomaly suggests precipitation and preservation of the chemical sediments in a progressively more oxygenated environment. The trace element composition of the Neoproterozoic sedimentary Fe and Fe-Mn oxides from Otjosondu, although significantly different from early Precambrian iron- and manganese-formations, are fully compatible with the "Snowball-Earth" scenario.

BG02 : MOam04 : G1 Evolution of Oxygen Distribution in Seawater

Graham Shields (gshields@science.uottawa.ca)
Ottawa-Carleton Geoscience Centre, University of Ottawa, P.O. Box 450 Stn. A, Ottawa, Canada

It is the received scientific wisdom that oxygen in the Earth's atmosphere and surface environment was scarce during the Archaean (4.0 Ga to 2.5 Ga) and subsequently rose stepwise during the Proterozoic. Geochemical and sedimentological evidence indicates that two major episodes of oxygenation occurred during the Palaeoproterozoic (ca. <2.5 Ga to 1.9 Ga) and during the Neoproterozoic (ca. 0.8 Ga to 0.6 Ga). Both oxygenation episodes coincide with major excursions in marine carbonate $\delta^{13}\text{C}$ of up to +18‰, and +11‰ to +16‰ PDB, respectively. Such high $\delta^{13}\text{C}$ is normally interpreted to arise from an increase in the amount of organic burial relative to

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carbonate deposition, which would also provide a mechanism for atmospheric oxygenation. However, the Precambrian $\delta^{13}\text{C}$ record reveals that these $\delta^{13}\text{C}$ excursions were rarely smooth rises to periods of sustained high values. Instead, stratigraphic fluctuations of >8‰, such as have never been recorded during the intervening 1.0 Ga, are observed. Many of these fluctuations can be related to sea-level changes. I would argue that such fluctuations are likely to be the result of redox stratification across the shallow shelf during these two episodes rather than to simple increases in the rate of organic burial. Ocean stratification has important implications for the interpretation of carbonate $\delta^{13}\text{C}$ over all of Earth's history, because the measured $\delta^{13}\text{C}$ of shallow marine carbonate will not always be representative of the whole ocean. This complication together with possible temporal variations in $\delta^{13}\text{C}$ of carbon input to the surface environment and carbonate-kerogen carbon isotopic discrimination make the connection between $\delta^{13}\text{C}$, carbon burial and oxygenation more tenuous. In this contribution, sedimentological, cerium anomaly, sulphur and carbon isotopic data will be discussed, which have provided additional support for widespread redox stratification during both periods of postulated oxygenation, and the late Neoproterozoic-Cambrian, in particular. Taken together, this evidence indicates that oxygen was not uniformly distributed throughout the water column during these two episodes as is generally the case today, but was instead concentrated solely in surface seawater, which would have become the only site of primary productivity. The concentration of oxygen in shallow seawater, as well as the expansion of oxygenated shallow water during transgression, would have provided a suitable and possibly essential environment for the evolutionary explosion of benthic fauna towards the end of the Neoproterozoic.

BG02 : MOam06 : G1 CO₂ Changes- Pacemaker of the Evolution

Günther Beckmann

(burkhard.kloppries@condea.de)¹,

Burkhard Kloppries, Hugo Hämmerle²,

Otto Inacker &

Peter Smolka (smolka@uni-muenster.de)³

¹ Condea AG, Paul Baumann Str. 1, D-45772 Marl, Germany

² NMI, Univ. Tübingen, Gustav-Werner Str. 3, D-72672 Reutlingen, Germany

³ Geo. Inst., Univ. Muenster, Corrensstr. 24, D-48149 Muenster, Germany

During the earth-history massive changes of the CO₂-content of the atmosphere have been observed. Consequently we describe the history of the atmosphere of the earth with equations that consider both background from chemistry, engineering and geology. It could be demonstrated, that times of accelerated atmospheric change coincide with times of accelerated evolution, i.e. an increased rate of forming of new species and disappearance of old ones. Together with microbiological evidence this suggests, that the extremely high gradient of present atmospheric change should be regarded as considerably more dangerous than in the past. The set of equations is relatively simple. It considers only massive global changes and effects. Nevertheless it yields insight into the atmospheric history and geological processes. All biological systems are aqueous systems. In these systems CO₂ is soluble. Since CO₂ participates directly or indirectly in many important reactions in cells, the CO₂-pressure in the cell is of prime importance. In systems characterized by low CO₂ partial pressures, such as many microbiological systems, moderate changes of the atmospheric CO₂ partial pressure cause a massive impact on chemical equilibria. Thus for many biological systems, the change (not necessarily the absolute value) of CO₂ partial pressure means a major environmental stress, caused by the close connection between atmospheric partial pressure and the interior of the cells. This environmental stress forces all species to adapt genetically. Microbiota and viruses can adapt much faster to the new situation due to their short life-span, resulting in a large number of new species. Statistically it has to be expected that among these new species there are at least some, that are incompatible with other hitherto existing biota (including "macrobiota"), i.e. threatening them as pests and diseases. This aspect of environmental change has not yet been paid sufficient attention.

BG02 : MOam10 : G1 Numerical Models of Phanerozoic O₂ Evolution: Carbon and Sulfur Isotope Records and the Physiological Response of Plants to Varying O₂/CO₂ Ratios

Robert Berner (robert.berner@yale.edu)¹,

Steven Petsch (spetsch@whoi.edu)²,

David Beerling (d.j.beerling@sheffield.ac.uk)³ &

Janice Lake³

¹ Dept Geology & Geophysics, Yale University, New Haven, CT 06520-8109, USA

² Dept. of Marine Chemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

³ Dept. of Animal and Plant Sciences, University of Sheffield, Sheffield S102TN, UK

The abundance and isotopic composition of marine carbon and sulfur-containing compounds can be used to reconstruct burial and weathering flux estimates for organic carbon [OC] and pyritic sulfur through time. Burial of OC and pyrite in sediments can be equated to net release of O₂ to the atmosphere. Atmospheric oxygen is consumed by the weathering of OC and pyrite in ancient sedimentary rocks (plus lesser oxidation of reduced C and S-containing gases from the metamorphic, volcanic and diagenetic decomposition of OC and pyrite). The balance between the rates of burial and weathering/oxidation constitutes the principal control on the evolution of oxygen over geologic time. Estimates of OC and pyrite burial, and the history of Phanerozoic O₂, have already been derived from records of the abundance of OC and pyrite in sedimentary rocks through time (Berner and Canfield, 1989). An independent approach uses the isotope records of marine carbonates and sulfates. Because both photosynthesis and biogenic pyrite formation discriminate in favor of light isotopes, OC and pyrite are isotopically depleted relative to their dissolved carbonate or sulfate sources. Reservoir effects dictate that OC and pyrite burial and weathering will influence the carbon and sulfur isotopic composition of seawater as recorded by carbonates and sulfates. A deconvolution of the carbonate and sulfate isotope records can be applied to generate histories of OC and pyrite burial and weathering which can in turn be converted into changes in atmospheric oxygen concentration over time. Recently, it has been shown that terrestrial plants and marine plankton vary carbon isotope discrimination in response to changes in the level of atmospheric O₂ (Berner et al., 2000). Elevated O₂ results in isotopically depleted biomass due to increased photorespiration, internal carbon dioxide recycling, and enhanced stomatal conductance. Using relationships between O₂ and the fractionation of carbon and sulfur isotopes during photosynthesis and sulfate reduction, a new modeled history of Phanerozoic O₂ variations has been generated from the carbonate and sulfate isotopic record (Berner et al., 2000). This history agrees with that derived earlier from rock abundance data and reveals appreciably elevated O₂ during Permian and Carboniferous times (350-250 Ma). This model result is consistent with geologic evidence for expansive coal burial, insect gigantism, and a newly-developed independent method of estimating paleo-atmospheric O₂/CO₂. The new method (Beerling et al., 2001) is based on laboratory growth experiments and the carbon isotopic analysis of fossil plants, and it independently supports a rise of O₂ concentration to about 35% during the Permian, followed by a subsequent fall to modern values for the remainder of the Phanerozoic. This novel method for estimating O₂/CO₂ ratios from plant isotopic composition shows promise as a new paleobarometer of atmospheric evolution over Phanerozoic time.

Berner RA & Canfield, DE, *Am. J. Sci.* **289**, 333-361, (1989).

Berner RA, Petsch, ST et al, *Science*, **287**, 1630-1633, (2000).

Beerling DJ, Lake JA et al, *Science (under review)*, (2001).

BG02 : MOam12 : G1 Biological and Environmental Consequences of Changing Oxygen Levels in the Late Palaeozoic

Andrew C. Scott (a.scott@gl.rhbc.ac.uk)¹ &

David J. Beerling (d.j.beerling@sheffield.ac.uk)²

¹ Geology Department, Royal Holloway, University of London, Egham, Surrey, TW20 OEX, U.K.

² Department of Animal and Plant Sciences, University of Sheffield, Sheffield, S10 2TN, U.K.

Fossil charcoal in late Devonian sediments indicates a minimum level of 13% (PAL) oxygen. The evolution of trees, and the spread of forests, in the late Devonian had major effects upon both oxygen and carbon dioxide levels. It is probable that oxygen levels had risen at least to present day levels by the earliest Carboniferous. Wildfires became

more frequent and widespread. Evidence from extensive charcoal deposits in Ireland, suggests the occurrence of ecologically catastrophic fires by the early Viséan. Giant scorpions in the late Viséan of Scotland also suggest high oxygen levels. The evolution of peat-forming arborescent vegetation in the Carboniferous, in tropical low-lying wetlands in particular, led to the sequestration of carbon on a widespread scale. A drop in carbon dioxide levels was enhanced in the Carboniferous by the burial of organic carbon as peat. Global cooling led to the build up of ice caps in the southern continents and the global fall of sea level, which in turn led to the extended occurrence of tropical peat-forming areas in Euramerica. Falling carbon dioxide levels are confirmed by using stomatal densities of land plants as atmospheric proxies. Increased oxygen levels, up to pO₂ of 35%, had a major effect on terrestrial ecosystems, allowing for more frequent fires in wetlands, as well as in upland areas. We present here new models of fire probability with varying oxygen levels and make comparisons with charcoal distribution data in Carboniferous sediments. Increasing oxygen levels may have been a stimulus for the evolution of flight in insects. Recent modelling supports the high oxygen levels at a time when gigantism in insects was widespread. The fluctuation of climate, atmospheric changes, and eustatic rises and falls in sea level appear to be inter-linked. It has been claimed that decreasing rainfall and increasing temperatures led to periods of tropical deforestation within the late Carboniferous. This in turn may have led to a rise of carbon dioxide levels leading to global warming and the melting of polar ice. Several arthropod groups continued to show gigantism in the later Carboniferous, such as the 2 m long *Arthropleura*. By the late Carboniferous and early Permian, insects with wingspans of more than 0.7 m indicate continued high oxygen levels. Climate change in the Permian caused major plant extinctions at a time of increasing carbon dioxide levels and falling oxygen levels. Fires were common in the Southern Hemisphere but were cooler, as indicated by the abundance in semifusinite in Permian Gondwana coals. The 'coal window' of the latest Permian and Early Triassic, together with the decrease in fire occurrence, indicates both climate and atmospheric changes with carbon dioxide levels rising and oxygen levels falling.

