

		ISSN 0016-7037 Volume 74, Number 15 August 1, 2010			
Geochimica et Cosmochimica Acta JOURNAL OF THE GEOCHEMICAL SOCIETY AND THE METEORITICAL SOCIETY					
EDITING EDITOR: FRANK A. PEEKER		EDITORIAL MANAGER: LINDA THOMER EDITORIAL ASSISTANT: KAREN KLEIN KATY SCYER			
WIREEDITOR: ROBERT H. NEEDLE, JR. PRODUCTION MANAGER: CHRIS AYER					
ASSOCIATE EDITORS:	ROBERT C. ALLEN ROBERT C. ALP YUKI ANDO CAROL ARONOW MARIKA BAIN-MATHIEW LIANG G. BERNING TAMARA S. BISHOP JAY A. BRONKHORST ALAN E. BURNISON DAVID J. BURNETT ROBERT H. BYRNE WILLIAM H. CARL THOMAS CHAPMAN JON CHAPMAN ANDRÉ COHEN CHRISTOPHER J. DICKERSON	ZORAN DRAK JAMES FARQUHAR FRANÇOIS A. FERT EDMUND GARLAND SUSAN GARLAND ETIENNE N. GORHAM TIMOTHY R. HALL H. ROBERT HARVEY GORDON R. HELL SUDIP R. HIRAJI GREGORY F. HIRSH JAMES HIRSH TAMARA HIRSH TAKESHI ISHIBASHI KAREN J. JARVIS KLAUS JARVIS	CHRISTIAN KÖRBER RUSSELL KOPPEL SPENCER M. KRACHER S. KRISHNAMURTHY ALEXANDER N. KRAUT GREGORY A. LARSON JONAS LUTZ THOMAS J. LIVING MICHAEL L. MACHUGA BERNARD MARET TOM MCCALLUM ANDRÉS MARRAS MARTIN A. MARIOTT JACK J. MCDONALD ALFONSO MONTI BENO MAYER	HIROSHI NAGAIWA MARTIN NAYAK PATRYA A. OTTAY ERIC H. OXBURGH EMERSON PAPPASABADINI SANDRA PIZZARELLO MARK RIBBISSON W. UWE RIBBEH PETER W. RICHARDS EDWARD M. RILEY KEVIN M. RYAN SARA S. RUSSELL E. J. RYANSON TOMAS A. SCHAUBER JACQUES SCHIFF THOMAS J. SHAW	JAP S. SPINKER DANIEL I. SPARKS DUSTIN A. STERNBERG MICHAEL J. TAYLOR PETER ULLICH DORIS VAN DER DAVID J. VANDER ROBERT J. WALKER LINDA A. WALKER JOHN WARD BOB A. WOODRUFF CHIN ZHANG
Volume 74, Number 15		August 1, 2010			
Articles					
I. H. CAMPBELL, R. J. SQUIRE: The mountains that triggered the Late Neoproterozoic increase in oxygen: The Second Great Oxidation Event 4187					
M. NOVAK, J. MIKOVA, M. KRACHLER, J. KOHLER, L. ERANOVA, E. PECHOVA, I. JACKOVA, D. FOTOVA: Radial distribution of lead and lead isotopes in stem wood of Norway spruce: A reliable archive of pollution trends in Central Europe 4207					
B. MIHRA, M. BOYANOV, B. A. BUNKER, S. D. KELLY, K. M. KEMNER, J. B. FEIN: High- and low-affinity binding sites for Cd on the bacterial cell walls of <i>Bacillus subtilis</i> and <i>Shewanella oneidensis</i> 4219					
F. N. SKOMRUCKI, S. KERRIST, K. M. ROSSO: Structure, charge distribution, and electron hopping dynamics in magnetite (Fe ₃ O ₄) (1 0 0) surfaces from first principles 4234					
L. WU, B. L. BEARD, E. E. RODEN, C. B. KENNEDY, C. M. JOHNSON: Stable Fe isotope fractionations produced by aqueous Fe(II)-hematite surface interactions 4249					
D. RENOCK, U. BECKER: A first principles study of the oxidation energetics and kinetics of realgar 4266					
M. XU, X. HU, K. G. KNATK, S. R. HOGSON: Dissolution kinetics of calcite at 50–70 °C: An atomic force microscopic study under near-equilibrium conditions 4285					
J. CAMA, L. ZHANG, J. M. SOLER, G. D. GUDICI, R. S. ARVIDSON, A. LETTIG: Fluorite dissolution at acidic pH: In situ AFM and ex situ VSI experiments and Monte Carlo simulations 4298					
R. H. BYRNE: Comparative carbonate and hydroxide complexation of cations in seawater 4312					
T. NOZAKI, Y. KATO, K. SUGIUE: Re–Os geochronology of the Imori Besshi-type massive sulfide deposit in the Sambagawa metamorphic belt, Japan 4322					
T. K. DALAL, G. RAVEZZA: Investigation of an early Pleistocene marine osmium isotope record from the eastern equatorial Pacific 4332					
<i>Continued on outside back cover</i>					

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



ELSEVIER

Available online at www.sciencedirect.com

Geochimica et Cosmochimica Acta 74 (2010) 4187–4206

**Geochimica et
Cosmochimica
Acta**
www.elsevier.com/locate/gca

The mountains that triggered the Late Neoproterozoic increase in oxygen: The Second Great Oxidation Event

 Ian H. Campbell^{a,*}, Richard J. Squire^b
^a *Research School of Earth Sciences, The Australian National University, Canberra 0200, Australia*^b *School of Geosciences, Monash University, Victoria 3800, Australia*

Received 25 November 2009; accepted in revised form 8 April 2010; available online 16 May 2010

Abstract

The consensus view is that the O₂ concentration of the Archean atmosphere was very low and that it rose to its present level of 21% in a series of steps, two of which dwarf the others in importance. The first, known as the Great Oxidation Event, occurred at ~2.4 Ga. It involved an increase in the relative abundance of O₂, which has been estimated at three orders of magnitude, and it is important because it led to the first surface weathering. The second, although less important in relative terms, involved the addition of 9×10^{17} kg of O₂ to the atmosphere, at least ten times as much as that required to produce the Great Oxidation Event. Its importance lies in the fact that it correlates with the rise of animals in the Ediacaran and Early Cambrian periods. Although it is widely accepted that an increase in atmospheric O₂ facilitated the appearance of animals at ~575 Ma, followed by the Cambrian Explosion ~50 Myr later, the cause of this increase remains controversial. We show that the surge in the O₂ level near the Precambrian–Cambrian boundary correlates with major episodes of continent–continent collision associated with Gondwana's amalgamation, including convergence between East and West Gondwana, which produced the 8000-km-long Transgondwanan Supermountains. The eroded roots of these mountains include the oldest lawsonite-bearing blueschists and eclogites, and ultra high-pressure metamorphic rocks. The sudden appearance of these low-thermal gradient, high-pressure metamorphic rocks implies that the Gondwanan orogenic zones were cooler and stronger than those associated with the assembly of earlier supercontinents and therefore capable of supporting higher mountains.

There is a log-linear relationship between relief and erosion rate, and a linear relationship between sedimentation rate and organic C burial. Taken together these two relationships imply a log-linear relationship between relief and C sequestration. We suggest that the Gondwanan supermountains were higher than those produced during the assembly of earlier supercontinents and that rapid erosion of these mountains released a large flux of essential nutrients, including Fe and P, into the rivers and oceans, which triggered an explosion of algae and cyanobacteria. This, in turn, produced a marked increase in the production rate of photosynthetic O₂. Rapid sedimentation during this period promoted high rates of burial of biogenic pyrite and organic matter generated during photosynthesis so that they could not back react with O₂, leading to a sustained increase in atmospheric O₂.

© 2010 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

The available evidence suggests that the O₂ content of Earth's early atmosphere was very low, probably less than 10⁻⁵ Present Atmospheric Level (PAL) and that it rose to

its present level in a series of steps (Canfield, 2005; Kump, 2008). Two of these steps are thought to dominate the rise of atmospheric O₂ (Kump, 2008). The first, initially recognized by Holland (2002) and called by him the Great Oxidation Event, occurred at about 2.4 Ga and was identified by the disappearance of redox sensitive minerals such as pyrite and uranite in sedimentary rocks, the appearance of red beds, and a sharp reduction of mass independent fractionation of ³³S (Farquhar and Wiing, 2003). Calculations

* Corresponding author. Tel.: +61 2 6125 4366.

E-mail address: Ian.Campbell@anu.edu.au (I.H. Campbell).

suggest that mass independent fractionation of ^{33}S can only occur if the O_2 content of the atmosphere is $<10^{-5}$ PAL (Pavlov and Kasting, 2002) and that the oxidative weathering required to produce red bed deposits requires atmospheric O_2 to exceed 1% PAL. The amount of O_2 that must be added to the atmosphere to produce this increase is $\sim 10^{16}$ kg. The second important step occurred in the late Neoproterozoic when atmospheric O_2 levels are thought to have increased from 5–10% PAL to 60–100% PAL (Canfield, 2005), requiring the addition of 9×10^{17} kg of O_2 . The first of these oxidation events, which we suggest should be called the First Great Oxidation Event (GOE-I) is important because it was during this event that atmospheric O_2 rose to the level required for the weathering of rocks. The importance of the second event, which we suggest should be called the Second Great Oxidation Event (GOE-II), is that it resulted in atmospheric O_2 rising to the level required for animal life. In relative terms GOE-I was the dominant event because during this event atmospheric O_2 rose by at least three orders of magnitude compared with less than two for GOE-II. However, in absolute terms GOE-II is the more important because it required the addition of almost 100 times the amount of O_2 to the atmosphere as GOE-I: 9×10^{17} kg compared with 10^{16} kg.

This paper concentrates on GOE-II, when atmospheric O_2 rose to the level required to support animal life. It is widely accepted that O_2 played a critical role in controlling first the appearance of animals at 575 Ma (Nursall, 1959; Berkner and Marshall, 1965; Knoll, 2003; Fike et al., 2006; Canfield et al., 2007) and later the Cambrian Explosion between 530 and 520 Ma (Cloud, 1968). The appearance of primitive animals probably occurred shortly after the O_2 concentrations in the upper oceans exceeded the critical level required to support them. Furthermore, because higher concentrations of O_2 promote increased cell and body size, and faster development (Berner et al., 2007) it is likely that the Cambrian Explosion occurred when oceanic O_2 levels exceeded a second threshold: one that allowed animals to flourish and multiply. There is now convincing evidence that oceanic O_2 concentrations rose during the Ediacaran to Early Cambrian periods (635–510 Ma) and that this increase coincided with the explosive rise of animals. However, the cause of this increase remains controversial.

Previously we argued that the rise of animals and subsequent Cambrian Explosion were triggered by rapid erosion of the Transgondwanan Supermountains, which were produced by the collision of East and West Gondwana (Squire et al., 2006a). We suggested that this caused a marked increase in the flux of critical nutrients such as Fe and P into the oceans that led to an explosion of primitive plant life, which provided the essential nourishment that promoted first the appearance of animals, and later the Cambrian Explosion. However, subsequent to publication of our earlier paper there have been a number of studies that show a step increase in O_2 in the late Neoproterozoic, which correlates with the rise of animals (Hurtgen et al., 2005; Fike et al., 2006; Canfield et al., 2007, 2008; Halverson and Hurtgen, 2007; Scott et al., 2008). Campbell and Allen (2008) have suggested that

step increases in atmospheric O_2 result from rapid erosion of supermountains produced during the assembly of supercontinents that increase the flux of nutrients into the oceans and promote photosynthetic production of O_2 . However, they did not explain why the assembly of the two Phanerozoic supercontinents, Pangea and Gondwana, produced increases in the absolute concentration of atmospheric O_2 that were an order of magnitude larger than earlier increases (Canfield, 2005; Kump, 2008).

In this paper we review the evidence for a late Neoproterozoic rise in O_2 and the competing hypotheses that attempt to explain it. We then document the timing of the orogenic events associated with the amalgamation of Gondwana and show that they correlate with the late Neoproterozoic rise in O_2 , whereas the alternate hypotheses do not. Finally we argue that the late Neoproterozoic and Phanerozoic step increases in O_2 are larger than earlier steps because they follow the sudden appearance of low-metamorphic-gradient, high-pressure and ultra high-pressure metamorphism from about 630 Ma (see Brown, 2007). We interpret the abrupt increase in the maximum pressure of orogenic-metamorphic belts to indicate that mountains produced by continent–continent collisions younger than about 630 Ma were higher than those produced prior to that time. We argue that higher mountains led to higher erosion rates and increased photosynthetic O_2 production during the late Neoproterozoic and Phanerozoic orogenic events compared with their earlier equivalents. Although we focus on the Gondwanan rise in atmospheric O_2 , we also show that the same hypothesis can explain a rise in O_2 of equivalent magnitude produced during the assembly of Pangea.

2. SOURCES OF OXYGEN

Three processes produce oxygen: dissociation of water by ultraviolet light, photosynthesis and biogenic pyrite formation. Negative feedbacks render the first of these processes ineffective and it can be neglected as a significant source of oxygen. The most important source of oxygen is photosynthesis, which occurs when plants induce a reaction between CO_2 and H_2O to produce organic C and O_2 , using light as the energy source. Organic C can also reduce sulfate to form biogenic pyrite, which produces almost four moles of O_2 for each mole of pyrite (Urey, 1952; Canfield, 2005). If the organic C or biogenic pyrite produced by these processes is buried during sedimentation, so that it cannot back react with O_2 , the concentration of O_2 in the atmosphere will increase. The principal sinks for O_2 are reduced volcanic gasses, weathering of organic C and pyrite in sediments, oxidation of reduced C and S gasses during burial diagenesis and metamorphism, and since ~ 575 Ma respiration, which in the modern World largely buffers O_2 produced by photosynthesis (Canfield, 2005). Oxidation of Fe and Mn in minerals other than pyrite is considered to be of lesser importance (Holland, 1978). At any time the relationship between O_2 sources and sinks is finely balanced. An increase or decrease in the concentration of O_2 in the atmosphere requires this balance to be disturbed by an external agent.

3. EVIDENCE FOR CHANGES IN O₂ LEVELS DURING THE PHANEROZOIC EON AND LATE NEOPROTEROZOIC ERA

There is no geochemical method that can be used to directly measure the O₂ concentration of the pre-Cambrian atmosphere and, as a consequence, changes in the O₂ concentration of the atmosphere must be inferred from changes in abundance of redox sensitive minerals, changes in the concentration of redox sensitive elements in sedimentary rocks and/or variations in C and/or S isotopes. These problems are compounded by the difficulty of projecting inferences drawn from deep-water sediments to the upper ocean and atmosphere. We begin by discussing the likely time scales for transfer of O₂ between these reservoirs.

3.1. Proterozoic atmospheric O₂ levels and the exchange of O₂ between reservoirs

Geochemical evidence has been widely interpreted to suggest that the Proterozoic oceans were anoxic (Poulton et al., 2004; Brocks et al., 2005; Canfield et al., 2007) and this observation has been used to infer that the O₂ concentration of the Proterozoic atmosphere was low (Canfield et al., 2007). Butterfield (2009) has pointed out that this interpretation is based on limited observations and that during Phanerozoic oceanic anoxic events birds, mammals, wildfires and aquatic reptiles were unaffected, showing that deep-water was not sequestering O₂ from the mixed layer or atmosphere and implying that the oceans were stratified and stable. Before we can accept the low O₂ interpretation for the Proterozoic atmosphere, based on the geochemistry of deep-water sediments, we must first establish the time scale for transfer for O₂ between the different O₂ reservoirs.

Atmospheric O₂ exchanges readily with O₂ in the mixed layer of the upper ocean, which today is about 100 m thick, by a combination of molecular diffusion and turbulent mixing. As a consequence, a change in the O₂ concentration in either of these reservoirs is rapidly transferred to the other, unless the mixed layer becomes O₂-saturated at the relevant temperature. The transfer of O₂ to the deep ocean, on the other hand, is by vertical turbulent diffusion and can be rapid or slow depending on the nature of the circulation active at the time. An example of O₂ being transferred quickly to the deep ocean is the rapid descent of cold, salty, oxygenated water at high latitudes in modern oceans. On the other hand an ocean basin or sub-basin can have an oxic upper mixed layer and be anoxic at depth and this condition can persist for an extended period. There are several examples of global anoxic oceans in the Phanerozoic, for example at end Permian, Mid-upper Cretaceous and late Devonian (Butterfield, 2009, and references therein). However, the time scales for Phanerozoic oceanic anoxic events are always less than 1 Myr (Jones and Jenkyns, 2001). In the modern oceans stable stratification is not a steady-state condition because vertical turbulent diffusion mixes the upper and lower waters on a time scale of order 1000–10,000 years (Ganopolski and Rahmstorf, 2001). Maintaining stable stratification in the oceans requires the thermohaline circulation to be blocked by connected landmasses or

surface forcing by the discharge of a large flux of fresh water into the oceans during melting of ice sheets (Ganopolski and Rahmstorf, 2001). The addition of fresh water to the oceans could induce global stratification of the oceans, but the expected time scale for such events is short, less than 10,000 years for melting of the Pleistocene glaciations. The time scale for melting of the extreme Proterozoic snowball Earth events is poorly constrained but was unlikely to exceed 1 Myr and is probably much less than that (Higgins and Schrag, 2003; Le Hir et al., 2009). As a consequence, although caution should be exercised in projecting short-term changes in O₂, inferred from sediments that formed below the upper ocean mixed layer to the atmosphere, changes in O₂ that persist in deep sediments on a global scale for extended periods of time, conservatively for more than 1 Myr, can be projected to the atmosphere with confidence. Therefore, we suggest that the widely held interpretation of low O₂ concentrations in the Proterozoic atmosphere (Canfield et al., 2007) is valid.

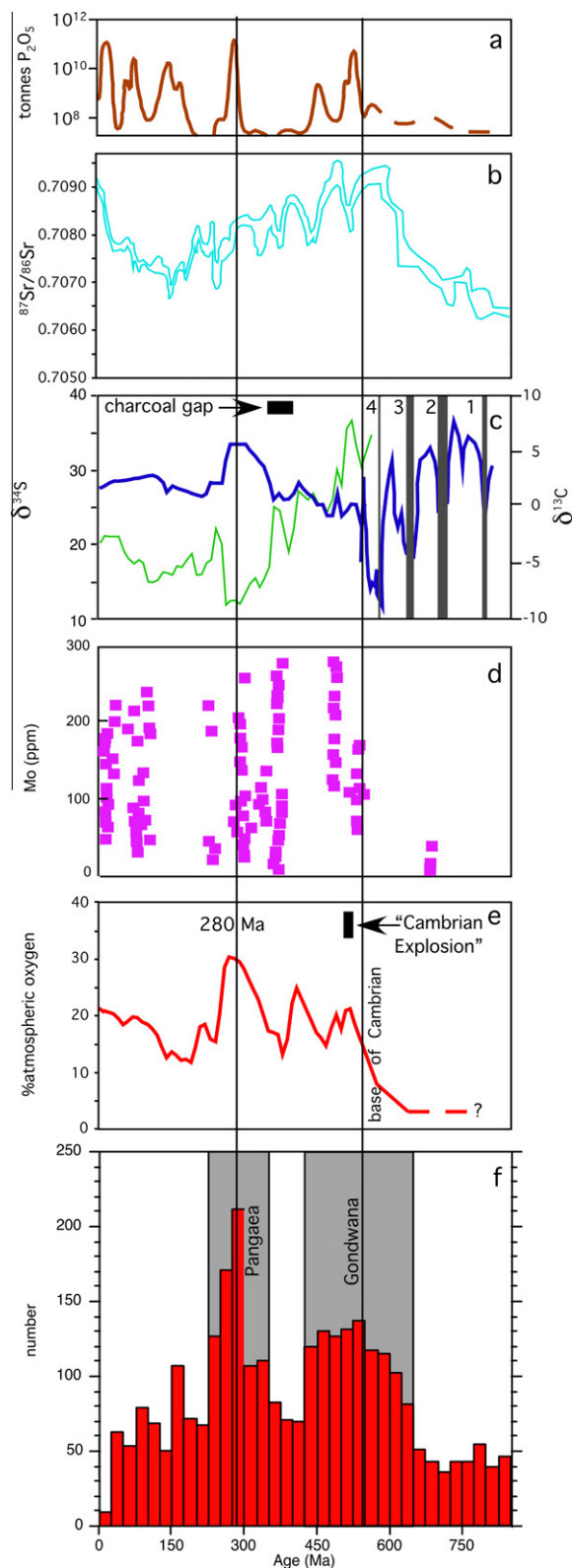
3.2. Phanerozoic changes in O₂ levels

From a low base in the Proterozoic eon, atmospheric O₂ levels rose to at least 60% Present Atmospheric Level (PAL), the minimum O₂ level required to sustain fire, by about 420 Ma (Kump, 2008). Berner (2006) modeled variations in atmospheric O₂ during the Phanerozoic eon, based largely on detailed variations in C and S isotopes (Fig. 1c). Features of his model include an increase in O₂ during the Cambrian period, a decline between 420 and 350 Ma, a step increase between 350 and 275 Ma (see also Beerling et al. (2002)), a further period of decline between 275 and 200 Ma and a gradual increase between 200 Ma and today (Fig. 1e). The charcoal record in sedimentary rocks supports these estimates of changing atmospheric O₂ over the last 420 Myr (Scott and Glasspool, 2006). As already noted, the first appearance of charcoal at 420 Ma requires atmospheric O₂ to have reached 60% PAL by that time. A gap in the charcoal record between 400 and 360 Ma (Kump, 2008) corresponds to the decline in O₂ over that period and it is followed by an increase in fossilised charcoal between 360 and 260 Ma (Berner et al., 2007) that coincides with the increase in O₂ during the Carboniferous and Permian periods. Finally, an increase in charcoal from 40 Ma to the present in North Pacific sedimentary rocks shows that atmospheric O₂ has increased over the last 40 Myr (Derry and France-Lanord, 1996). The case for an increase in atmospheric O₂ between 360 and 260 gains further support from gigantism in several arthropod groups and reptile like animals over that period (Graham et al., 1995; Dudley, 1998), which is attributed to elevated O₂ levels. Similarly an increase in mammal body size through the Tertiary period has been attributed to rising levels of O₂ (Falkowski et al., 2005).

3.3. Cambrian and late Neoproterozoic increases in O₂ levels

Variations in atmospheric O₂ levels during the Cambrian and late Neoproterozoic intervals are of special interest in the current context. Several detailed studies, three of

which use different methodologies, suggest that the Cambrian increase in atmospheric O₂, noted by Berner (2006), started during the late Neoproterozoic era. Fike et al. (2006) used high-resolution carbon and sulfur isotope data



from the late Neoproterozoic marine sedimentary rocks from the Huqf Supergroup in Oman to identify two increases in oceanic O₂ levels during the Ediacaran period, which were identified from increases in $\Delta^{34}\text{S}$, the difference between sulfate $\delta^{34}\text{S}$ and the most negative $\delta^{34}\text{S}$ value in pyrite. The first, following the Marinoan Glaciation (636–663 Ma, Halverson et al., 2005), is based on a gradual increase in $\Delta^{34}\text{S}$ from 1‰ to 12‰ at 636 Ma to ~35‰ at 580 Ma, requiring an increase in marine seawater sulfate from less than 200 μM to greater than 200 μM . The second occurred between 548 and 542 Ma and is recognized from an increase in $\Delta^{34}\text{S}$ to 50‰. Values of $\Delta^{34}\text{S}$ above 46‰ are unknown in the Proterozoic eon and have been interpreted to suggest bacterial sulfur disproportionation in which intermediate-valency sulfur species are split into $\delta^{34}\text{S}$ -enriched sulfate species and $\delta^{34}\text{S}$ -poor hydrogen sulfide, which requires an increase in the level of oxidation. A third increase was postulated by Fike et al. (2006) following Gaskiers Glaciation at ~580 Ma. It was identified from a prolonged negative excursion in $\delta^{13}\text{C}$ in marine carbonates, called the Shuram Excursion, in which values fell to well below mantle values for at least 25 Myr. However, the Fike et al. (2006) interpretation of Shuram Excursion has been discredited by Bristow and Kennedy (2008) on the basis of dissolved organic C mass balance and the scale of the event, which they argue cannot have lasted more than

Fig. 1. The timing of orogenic events associated with the assembly of Pangea and Gondwana determined from U/Pb detrital zircon ages compared with variation in atmospheric O₂, P₂O₅ in phosphate deposits, Mo concentrations in black shales, and S, C and Sr isotopes through time. (a) Variation in the tonnes of P₂O₅ in phosphate deposits through time (Cook and Shergold, 1984). (b) Variation in ⁸⁷Sr/⁸⁶Sr in seawater through time (Shields and Veizer, 2002). (c) Variations in ¹³δC in marine carbonates (blue) and ³⁴δS in sulfate (green) from Berner (2006), ¹³δC data between 800 and 550 Ma from Halverson et al. (2005). Black lines correspond to ice ages. 4 = Gaskiers Glaciation, 3 = Marinoan Glaciation, 2 = Sturtian Glaciation, 1 = Bitter Springs stage. (d) Variations in the Mo concentration in black shales (Scott et al., 2008). (e) Estimated variations in % atmospheric O₂ through time. The general form of the figure follows Berner (2006) but the extension into the Neoproterozoic era is based on the evidence of Canfield et al. (2008) and Fike et al. (2006). Canfield et al. (2007) estimated the O₂ content of the Early Cambrian atmosphere to be at least 15% of PAL, Bergman et al. (2004) suggested 25% PAL, whereas others (Hurtgen et al., 2005; Halverson and Hurtgen, 2007) suggested a value slightly less than present day levels. (f) Laser ablation ICP-MS U/Pb ages for 6968 detrital zircons younger than 850 Ma. The data for Asia, Europe, and North and South America are from 5249 zircons separated from sands collected near the mouths of 40 major rivers (Campbell and Allen, 2008) and are supplemented by SHRIMP zircon data from Australian sand dunes (Pell et al., 1997) (*n* = 1136), and from Antarctic Paleozoic sediments (Goodge et al., 2004; Flowerdew et al., 2007) (*n* = 583). The timing of orogenic events is determined by geochronology and, as a consequence, the compilation of U/Pb dates can be used to identify the principal tectonic events that have affected Earth. The compilation picks out the Pan-African and Hercynian-Alleghanian orogenies associated with the assembly of the Gondwana and Pangea supercontinents, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

800 kyr. Bristow and Kennedy (2008) and Knauth and Kennedy (2009) attribute the Shuram Excursion to diagenetic alteration.

Nevertheless the overall conclusions of Fike et al. (2006), which are based on an increase in $\Delta^{34}\text{S}$ in the Ediacaran ocean, imply that sulfate was replacing sulfide as the dominant S species in late Neoproterozoic oceans, are valid. Analyses of sulfate and pyrite in sedimentary rocks from South Australia and Namibia gave similar results and are also interpreted to indicate an increase in atmospheric O_2 to roughly Phanerozoic levels by the end of the Neoproterozoic era (Hurtgen et al., 2005; Halverson and Hurtgen, 2007).

Canfield et al. (2007) used a different method to demonstrate an increase in ocean O_2 in the Ediacaran period. They measured variations in the fraction of highly reactive Fe (FeHR) to total Fe (FeT) in late Neoproterozoic sediments from Newfoundland, Canada to demonstrate an increase in oxidation state. A fraction of FeHR/FeT less than 0.38 is indicative of oxic conditions. They found evidence for negligible O_2 in the deep oceanic water during the 580 Ma Gaskiers Glaciation, but showed that it increased sharply to at least 15% PAL following this glaciation. Similarly Shen et al. (2008) documented a sharp drop in FeHR/FeT from mostly greater than 0.38 to less than 0.25 in black pyrite-rich shales for the Northwest Territories, Canada, which they constrain to have occurred between 580 and 610 Ma. A more extensive study of late Neoproterozoic sedimentary rocks deposited below the storm-wave-base by Canfield et al. (2008), in which over 700 samples were analyzed from 34 formations and 13 location with ages between 850 and 530 Ma, found that samples frequently had FeHR/FeT below 0.38 indicating that oxic bottom waters were common. Although both anoxic and oxic deep-water are indicated throughout the late Neoproterozoic era, there is a general increase in the fraction of deep-water sedimentary rocks with FeHR/FeT less than 0.38 through time. FeHR/FeT for sedimentary rocks older than 650 Ma are generally more than 0.38 (i.e., conditions were anoxic), but become sub-equal to 0.38 between 650 and 580 Ma, and were overwhelmingly less than 0.38 (i.e., oxic conditions) between 560 and 580 Ma. Finally, the conclusion that upper ocean O_2 levels began to rise, starting at about 650 Ma, is supported by a marked increase in redox sensitive Mo in sulfide-bearing black shale between 663 and 551 Ma (Fig. 1d) (Scott et al., 2008).

Although the absolute concentrations of O_2 in the Neoproterozoic oceans and atmosphere are not well constrained, these five studies, taken together, provide convincing evidence for a significant increase in oceanic O_2 levels during the Ediacaran period. The best estimates suggest that atmospheric O_2 concentrations rose from 5–10% PAL at 650 Ma (Canfield, 2005; Kump, 2008) to 60–80% PAL by 500 Ma (Canfield, 2005; Berner, 2006). Fig. 1a shows a plot of the estimated O_2 concentration of the atmosphere over the last 850 Myr, based on the Berner (2006) model for the Phanerozoic eon, but modified to accommodate the constraints suggested by Fike et al. (2006), Hurtgen et al. (2005), Halverson and Hurtgen (2007) and Canfield et al. (2007) for an increase in O_2 over the Ediacaran period. Although details of this rise in O_2 are uncertain the widespread evidence of

anoxia in the pre-Neoproterozoic oceans, referred to earlier, suggests that the O_2 concentrations in the oceans and atmosphere were low (Poulton et al., 2004; Brocks et al., 2005; Canfield et al., 2007). This conclusion is supported by the reappearance of small Fe formations associated with the snowball Earth glaciations, which suggest that upper ocean O_2 levels had fallen to the low levels required for the transport of Fe as Fe^{2+} , a condition not seen since the disappearance of banded iron formations at 1.85 Ga, although this could be due to short-term anoxia in the oceans if they were completely covered by ice as suggested by Kirschvink (1992). As already noted, the appearance of charcoal at 420 Ma requires atmospheric O_2 to have reached 60% PAL by that time.

4. HYPOTHESES FOR THE RISE IN O_2

4.1. Hypotheses based on evolution

Several evolutionary mechanisms have been suggested to explain the Ediacaran-Early Cambrian rise in O_2 . For example the rise in O_2 has been attributed to the advent of muscular unidirectional guts in animals enabling rapid transportation of organic matter, in the form of dense fecal pellets, to the sea floor where it could be buried and 'stored' (Logan et al., 1995). The problem with this hypothesis is that macrozooplankton, the first animal that was large enough to produce fecal pellets that would sink rapidly, did not appear until after ~ 543 Ma based on molecular-clock data (Peterson et al., 2005), or after ~ 520 Ma based on fossil evidence (Chen and Zhou, 1997; Vannier and Chen, 2000). Furthermore, studies of modern sediments show that zooplankton fecal pellets are a minor component of the organic C flux (Turner, 2002). Most of the organic C rain is transferred from the epipelagic to the sea floor by aggregation of phytoplankton or marine snow, which do not appear to undergo consumption while sinking through the water column (Turner, 2002) and renders the improved efficiency of an animal driven biological pump unnecessary (Butterfield, 2009).

Sperling et al. (2007) suggested that the evolution of sponges many tens of millions of years prior to macrozooplankton may have been responsible for the late Neoproterozoic rise in oxygen levels. Sponges feed principally on dissolved organic carbon, part of which is oxidized during respiration and part of which is excreted as insoluble C. The significance of this process is that dissolved organic C is not readily sequestered in sediments whereas the fraction that is converted to insoluble C can be sequestered. Sponges are highly efficient at circulating water through their bodies and a large modern sponge can process its own volume in 10–20 s. However, because sponges are animals, this process consumes O_2 . Whether the insoluble C secreted by the sponges is sufficient to offset the O_2 they consume has yet to be demonstrated quantitatively. More importantly, animals including sponges cannot have driven the rise in O_2 required for their existence.

An alternate biological trigger for rising O_2 levels is the emergence of a land-based biosphere, which may have

helped to accelerate rock weathering. Kennedy et al. (2006) suggested that the rise of a land-based biosphere led to a marked increase in the rate of clay production through the breakdown of tectosilicates, and that erosion of this material led to high rates of C burial and thus oxygen production. Kennedy et al. (2006) noted a marked increase in the ratio of phyllosilicates to quartz in mudstones between 750 and 500 Ma that they attributed to the expansion of land-based biota, which they correlated with the rise of animals. The discovery of lichen-like fossils in marine phosphates from southern China, which are bracketed by U/Pb dating to have been deposited between 551 to 635 Ma, but based on fossil evidence are more likely to have formed between 551 and 580 Ma, support the hypothesis that primitive soil biota preceded vascular plants on land (Yuan et al., 2005). However, soil biota may have made their appearance on land much sooner and well before the appearance of animals at 575 Ma. Pave (2002) documented biological structures in non-marine 1.2–1.0 Ga siliciclastic rocks from Scotland, including the occurrence of wrinkle structures, and morphological features similar to microbial crusts, which they attributed to land-based biota. This conclusion is supported by protein sequence analyses (Heckman et al., 2001), which suggest that green algae and fungi were present on land by 1000 Ma. Although the Kennedy et al. (2006) hypothesis is difficult to test because the timing of the appearance of primitive soil biota is poorly constrained, the appearance of soil biota in the Mesoproterozoic or Neoproterozoic eras must have accelerated soil production and erosion, and provided an additional source of organic C to compliment organic C production in the oceans.

Another plausible evolutionary hypothesis for the rise in late Neoproterozoic O₂ is an increase in the abundance of large, single-celled eukaryotic algae (phytoplankton), which occurred at that time (Falkowski and Knoll, 2007; Falkowski and Isozaki, 2008). However, multicellular red algae are known from at least 1200 Ma (Butterfield et al., 1990) and single-celled eukaryotic algae logically existed even earlier. The observed increase in eukaryotic algae could be due to better preservation. For example, tougher animal-resistant species may have become dominant in the late Neoproterozoic era. More likely, the increase in phytoplankton was due to an increase in the supply of nutrients reaching the oceans, as suggested by Squire et al. (2006a). Alternatively, an increase in the cell size of phytoplankton from picoplankton to (0.2–2.0 μm) to export-prone net-plankton (2–200 μm), in response to the emergence of grazing zooplankton, may have increased the efficiency of the biological pump (Butterfield, 2009). Net-plankton aggregate and sink faster than picoplankton. The cell size of Ediacaran phytoplankton is a matter for speculation, and the occurrence of C-rich shale in sequences that formed as much as 2.0 Gyr before the appearance of animals suggests that this is not a first-order consideration.

4.2. Snowball Earth hypothesis

The Neoproterozoic era is characterized by two extreme global glaciations, the Sturtian and Marinoan Glaciations,

which are commonly referred to as snowball Earth events (Kirschvink, 1992; Hoffman et al., 1998). Although the snowball Earth hypothesis is controversial because it requires the equatorial oceans to be ice-bound, there is general agreement that ice extended to the sea at low latitudes (Allen and Etienne, 2008). Halverson and Hurtgen (2007) attribute the rise in O₂ during the middle Ediacaran period (~600 Ma) to a catastrophic increase in the rate of erosion in a post-glaciation, CO₂-rich, ultra-greenhouse environment that followed the 663–636 Ma Marinoan Glaciation. They argue that this led to high rates of nutrient delivery into Earth's oceans, and to enhanced photosynthesis and organic C burial. Evidence used to support their interpretation included the presence of abundant organic C-rich post-glacial sedimentary rocks that are broadly coincident with a rise in the marine ⁸⁷Sr/⁸⁶Sr record (Fig. 1c). Although enhanced post-glacial erosion may have contributed to the late Neoproterozoic rise in O₂, especially its onset, it cannot be the driving mechanism because the rise in O₂ continued to about 515 Ma, well beyond the youngest Neoproterozoic glaciation (Gaskiers, Fig. 1c) at 580 Ma. Furthermore, the 723 Ma Sturtian Glaciation, which preceded the Marinoan Glaciation (Halverson et al., 2005), did not produce a documented increase in atmospheric O₂ (Fig. 1c).

4.3. Tectonic hypothesis

There is a positive correlation between sedimentation rates and the C content of sedimentary rocks in oxic oceans (Bernier and Canfield, 1989; Stein, 1990). There are two reasons for this. First, rapid sedimentation occurs during periods of rapid erosion when the flux of essential nutrients into the oceans is high, which promotes the growth of primitive plants in the oceans. Second, high sedimentation rates favor the preservation of organic C by reducing the time it spends lying on the sea floor in an oxic ocean (Stein, 1990). Furthermore, high surface organic C production rates lead to a high flux of C through the ocean, which lowers the oxygen content of the water through which it sinks and increases the fraction of organic C reaching the sea floor. The modern sedimentary rocks with the highest C contents are found near the mouths of modern rivers where the terrigenous input is high, areas of rapid sedimentation such as turbidites (Stein, 1990) and areas of nutrient upwelling such as the Peru–Chile coast (Bernier, 1982). Of these, deltaic sediments constitute the most important sink for modern C. Bernier (1982) estimates that 1.3×10^{11} kg of 1.57×10^{11} kg per year or 83% of organic C buried in modern sediments is stored in deltaic sediments. The organic C content of continental shelf sediments deposited away from rivers is low (Bernier, 1982). These observations show the importance of the supply of terrigenous nutrients in controlling the rate organic C production and storage in sediments, and therefore photosynthetic O₂ production.

It has been suggested that enhanced sedimentation rates during periods of continental break-up (Knoll et al., 1986; Derry et al., 1992; Lindsay and Brasier, 2002) or during the opening and closing of an ocean basin (Des Marais et al., 1992) could lead to increased C burial and an increase

in atmospheric O₂. However, the highest sedimentation rate in Earth's history occur not during periods of continental break-up but during the erosion of mountains produced by continent–continent collisions, especially those associated with supercontinent assembly (Squire et al., 2006a).

4.4. Continental growth and supermountains

Campbell and Allen (2008) have argued that the principal sources for atmospheric O₂ are burial of organic carbon and pyrite in sediments and that the principal sinks are reduced volcanic gasses. They suggest that atmospheric O₂ has increased over Earth history because the balance shifted from reduced volcanic sinks in the Archean to oxidizing sedimentary sources during the Proterozoic. Volcanism has logically declined over Earth history in response to the declining contribution from radioactivity to the mantle's heat budget while the contribution from sedimentary sources has increased. Two factors contribute to the latter. First, most models for growth of the continental crust suggest that it has grown through time and that growth was only ~50% complete by the end of the Archean (McLennan and Taylor, 1982; Wang et al., 2009). Second, the abundance of pillow basalts in the Archean and the relative paucity of sedimentary rocks, most of which are volcanogenic, suggest that the continental crust was largely below sea level. During the Archean, basalts dominated the supracrustal sequences with sedimentary rocks a minor component. By 2.5 Ga this situation reversed and O₂ producing sediments dominated the supracrustal sequences at the expense of reducing basalts. This fundamental change in the nature of supracrustal rocks coincides with Holland's (2002) Great Oxidation Event. Superimposed on this overall increase in O₂ are a series of steps, which Campbell and Allen (2008) correlated with the amalgamation of supercontinents.

Sedimentation rates are a function of denudation rates. A remarkable log-linear correlation between relief and denudation, over almost three orders of magnitude in several studies, shows that relief is the dominant factor controlling erosion rates (Vance et al., 2003, and references therein), and therefore the supply of nutrients to the oceans and organic C burial rates. High rainfall, soil biota and high atmospheric CO₂ promote the mechanical, biological and chemical breakdown of rocks respectively but, in the absence of relief, do not give rise to high rates of erosion and sedimentation. Wind and continental glaciations are the only effective agents of erosion on a flat surface. If the log-linear relationship between relief and denudation rate is combined with the linear relationship between sedimentation rate and C burial, and if it is assumed that sedimentation rate is a function of denudation rate, *there must be a log-linear relationship between relief and C sequestration.*

The highest average global erosion rates occur during the formation of supercontinents. Squire et al. (2006a) suggested that continent–continent collisions that occurred during the amalgamation of supercontinents produced large mountain ranges that eroded rapidly, releasing a large flux of critical nutrients such as P and Fe into the oceans. P is the bio-limiting nutrient in the oceans (Broker, 1982) and

Fe is required to facilitate the electron transfer reactions essential for N-fixing bacteria (Falkowski, 1997). The increased supply of these nutrients in the upper oceans led to an explosion of algae and cyanobacteria, and to the production of photosynthetic O₂. Because orogenic episodes are periods of high sedimentation it is likely that a high fraction of the organic C and biogenic pyrite produced were buried so that they could not back react with O₂, leading to sustained increases in atmospheric O₂. Campbell and Allen (2008) pointed out that five of six recognized step increases in atmospheric O₂ correlate with assembly of the five known supercontinents: Pangea, Gondwana, Rodinia, Nuna and Superia-Sclavia. The sixth rise coincides with an orogenic event at 2.45 Ga (Fig. 1), which Pehrsson and Jefferson (2009) suggests is a previously unrecognized supercontinent called Nunavutia. A slight increase in atmospheric O₂ over the last 40 Myr correlates with the collision between India and Eurasia (Derry and France-Lanord, 1996).

Berner and Canfield (1989) have argued that the organic C and pyrite burial rate is independent of sedimentation rate. Their reasoning is that sedimentary rocks are derived from erosion of older sedimentary successions and that burial of C and pyrite during a given cycle of erosion and sedimentation is balanced by oxidation of C and pyrite during erosion of the older sedimentary source. This argument may be valid for sedimentation during anorogenic periods but it is not valid for sedimentation during an orogenic event for two reasons.

First, as Berner and Canfield (1989) have shown, the C content of sedimentary rocks increases with the sedimentation rate. Therefore the Berner and Canfield (1989) argument is only valid if the older, eroded and new sedimentary rocks were deposited at the same rate. If the new sedimentary units were deposited faster than the old ones that were eroded to form them, the new successions will have a higher C content. Conversely, if the new sedimentary units were deposited at a slower rate than the new ones they will have a lower C content. Because of the log-linear relationship between relief and erosion rate mentioned previously, global sedimentation rates must be higher during orogenic periods than during anorogenic periods. If, as is likely, a high fraction of the sedimentary rock that was eroded during an orogenic period was derived from average or low-deposition-rate, low-C successions, the C content of the rapidly deposited orogenic sequences will be higher than the global average. The converse is true for low-depositional-rate anorogenic sedimentary rocks. That is, on average, orogenic sedimentary rocks should be C-rich, and anorogenic sedimentary rocks C-poor, relative to the global average.

Second, the Berner and Canfield (1989) hypothesis ignores the contribution of igneous rocks to sedimentary cycles. Although erosion of igneous material may make a minor contribution to anorogenic sediments it is expected to make a significant contribution to orogenic sediments. This is because major orogenic events are accompanied by significant igneous activity, as both granitic intrusions that stiffen the spine of mountain belts, and as complimentary volcanism. Therefore, orogenic sedimentary cycles include both recycled sedimentary detritus and new

sedimentary detritus derived from weathering of igneous rocks. The global sedimentary mass has therefore increased though Earth history for two reasons: first because the mass of the continental crust has increased through Earth history (McLennan and Taylor, 1982), and second, because igneous material has been continually eroded and incorporated into the sedimentary mass. The latter will be more important during orogenic periods than during anorogenic periods.

5. THE RISE IN O₂ DURING THE LATE NEOPROTEROZOIC AND CAMBRIAN INTERVAL

Of special interest in the context of this study is the increase in atmospheric O₂ associated with the assembly of Gondwana (Fig. 2). We argue that rapid erosion of the mountains generated during Gondwana's amalgamation produced an enhanced supply of nutrients into rivers, lakes and oceans, which led to an explosion of primitive plant life and to a marked increase in the production of O₂. The marked increase in seawater ⁸⁷Sr/⁸⁶Sr in the late Neoproterozoic to the highest values recorded in Earth's history (Fig. 1b) shows that this was a period of rapid continental erosion, as does the widespread occurrence of phosphate beds in the Cambrian (Cook and Shergold, 1984) (Fig. 1a). Equally important, increased sedimentation ensured that a high fraction of the complimentary organic C and pyrite were buried so that they could not back react with O₂. Erosion of the Transgondwanan Supermountains, generated by the collision of East and West Gondwana, produced >100 million km³ of sedimentary rocks (2.5 × 10²⁰ kg), enough material to cover the USA with a layer of rocks 10 km thick (i.e., the Gondwana Superfan System, Squire et al., 2006a), so the amount of organic C and biogenic pyrite produced and buried during this period must have been enormous.

The validity of our hypothesis depends on two critical factors:

1. The timing of the amalgamation of Gondwana and the formation of the large mountain ranges, including the Transgondwanan Supermountains, relative to the late Neoproterozoic rise in O₂.
2. There should be evidence of abundant C-rich Gondwanan sedimentary rocks to provide the complimentary organic C reservoir required for the rise in O₂.

We therefore briefly review the evidence for when and where large mountain ranges grew during Gondwana's amalgamation and for the existence of sedimentary rocks rich in C.

5.1. The size of the mountains and timing of their formation

Abundant evidence exists for several large mountain ranges forming in Gondwana between about 650 and 515 Ma but confusion remains as to whether the continent-continent collisions that created them were the result of convergence between East and West Gondwana (Stern, 1994; Jacobs and Thomas, 2004; Squire et al., 2006a),

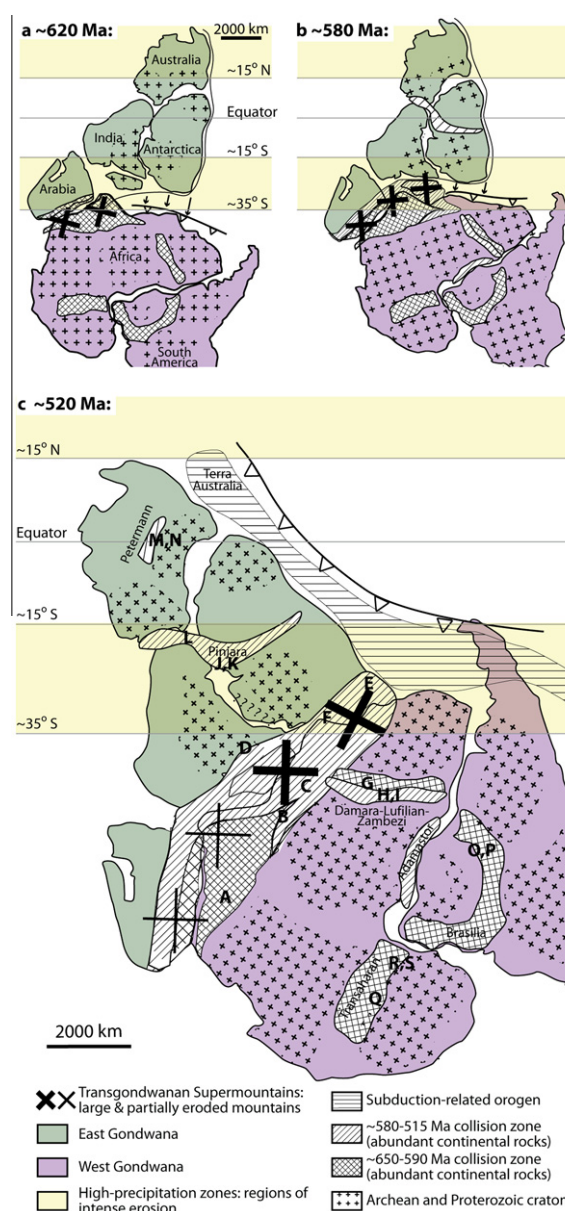


Fig. 2. Sketch maps showing the episodic growth of the Gondwanan supermountains. (a) Initial collision zones between about 650 and 620 Ma. (b) Uplift and exhumation was more widespread from about 580 Ma, during which time the Transgondwanan Supermountains, the largest of the Gondwanan mountain ranges, grew largely within the 'high precipitation zone' between about 15° and 35° latitude. (c) Even during the final stages of orogenesis the active parts of the Transgondwanan Supermountains stayed in or near the 'high precipitation zone'. Also, mountain ranges developed along Gondwana's outer margins became increasingly important during the final stages of supercontinent amalgamation. Letters A to S show the locations of data used in Table 1. Modified after Squire et al. (2006a), Cawood (2005) and Squire et al. (2006b).

North and South Gondwana (i.e., Australia, Antarctica and perhaps southern-most Africa colliding with India, Madagascar and Africa, Meert, 2003; Collins and Pisarevsky, 2005; Fitzsimons and Hulscher, 2005; Cawood

and Buchan, 2007), or a succession of smaller collisional events (Veevers, 2003). Although we support the proposition involving convergence between East and West Gondwana, the purpose of this discussion is not to determine which of these hypotheses is correct, but to highlight that large volumes of rocks from Gondwana's late Neoproterozoic orogens were deeply buried and rapidly exhumed between about 650 and 500 Ma. A summary of the principal data used in this discussion is provided in Table 1.

The following discussion focuses primarily on evidence for eclogite-facies metamorphic rocks and associated granulites in each of the principal Gondwanan orogens, plus the timing and rates of cooling of those rocks. This is because eclogites and granulites occur in the root zones of modern mountain chains, as well as the deeper parts of subduction zones, and are good indicators of crustal-thickening events (e.g., Maruyama et al., 1996; Zang et al., 2009). Himalayan-style mountain chains, generated by continent–continent collisions, are generally taller and larger in volume than Andes-style ranges generated by subduction-related processes (Hyndman, 2005), which is important in the context of delivering organic C to the ocean. Therefore, we also review the evidence for involvement of oceanic crust and magmatic arcs that enable the styles of the mountain ranges to be determined. To begin, we discuss the evidence for mountain-building along the 8000-km-long and up to 1500-km-wide East African – Antarctic Orogen (i.e., the root zone to the Transgondwanan Supermountains), which is the largest of the Gondwanan Orogens, then follow with descriptions of the others.

5.1.1. Orogens comprising the Transgondwanan Supermountains

The 2500-km-long Keraf-Kabus-Sekerr Suture formed during the late Neoproterozoic when northern Africa's Saharan Metacraton collided with the Arabian-Nubian Shield (Abdelsalam et al., 2002, 2003). Granulite-facies migmatitic rocks from the Sabaloka region, Sudan, have metamorphic assemblages consistent with burial to pressures of 6–8 kbar and temperatures of 600–800 °C, and are interpreted to reflect depths up to about 30 km (Kröner et al., 1987). Although granulite peak metamorphic conditions were initially dated at ~700 Ma (Kröner et al., 1987), recent U–Pb monazite ages suggest it could be as young as 620 Ma (Küster et al., 2008). ^{40}Ar – ^{39}Ar biotite and hornblende ages of about 580 Ma from deformed granites in northern Sudan indicate that the granulites were uplifted and cooled soon after peak burial (Abdelsalam et al., 1998). Other evidence for the Keraf-Kabus-Sekerr Suture representing a major continent–continent collision zone involving closure of an ocean basin includes the occurrence of Neoproterozoic juvenile successions such as dismembered ophiolite belts, arc assemblages and A-type granitoids (Abdelsalam et al., 2003).

The late Neoproterozoic amalgamation of southern India, Madagascar and East Africa (i.e., the Mozambique Belt) is controversial. Several authors have postulated that this unusually wide (up to 1500 km) orogen formed during accretion of outboard terranes and involved relatively minor continent–continent collisions (e.g., Azania and proto-

Madagascar) between about 655 and 610 Ma (Meert, 2003; Collins and Pisarevsky, 2005; Cawood and Buchan, 2007; Maruyama et al., 2009; Santosh et al., 2009). However, a growing body of metamorphic and structural data suggest that the region experienced a major episode of crustal-thickening between about 580 and 550 Ma (Boger and Miller, 2004; Sommer et al., 2005; Cutten et al., 2006; Hauenberger et al., 2007; Rossetti et al., 2008; Bingen et al., 2009). This is confirmed by the presence of garnet-pyroxene-bearing granulites in Mozambique that indicate burial of these rocks to depths of up to 55 km between about 580 and 550 Ma; reaction textures and garnet zoning associated with these rocks have been used to suggest that they were rapidly exhumed soon after peak metamorphism (Engvik et al., 2007). Evidence also exists for a younger crustal-thickening event in the region. In Malawi, ~530–500 Ma garnet-bearing gneisses were buried to ~60–70 km (17–18 kbar) then rapidly exhumed (Ring et al., 2002), and in southern India eclogites (about 19 kbar) and high-pressure granulites (about 12 kbar) were generated at about 535 Ma then quickly uplifted (Santosh and Sajeve, 2006; Santosh et al., 2009). The presence of fault-bounded slices of ophiolites and arc volcanic rocks throughout the Mozambique Belt supports closure of an ocean basin during a continent–continent collision.

Although the Antarctica ice cap and South Africa's Karoo Sandstone now cover most of the rocks generated along the 3000-km-long boundary between the Kalahari and East Antarctic Cratons, studies of the sparse outcrops from the region suggest that they represent the products of a major continent–continent collision zone associated with Gondwana's amalgamation. In the Shackleton Range, East Antarctica, garnet-olivine-bearing ultramafic rocks have metamorphic assemblages consistent with burial to depths of about 70 km and garnet-whole-rock Sm–Nd isochron ages of 525 ± 5 and 520 ± 14 Ma (Romer et al., 2009). In western Dronning Maud Land, East Antarctica, high-pressure granulite-facies rocks with interpreted burial depths of 47–52 km (Board et al., 2005) are also present. Garnet-omphacite-bearing mafic eclogite boudins are also present among these granulites, which were buried to depths of ~47–52 km, but are of uncertain (Mesoproterozoic to 540 Ma) age. Rb/Sr biotite cooling ages of 500 ± 10 Ma in the Shackleton Range indicate that rapid exhumation occurred soon after peak metamorphism (Zeh et al., 1999). The presence of the ultramafic rocks in the Shackleton Range suggests oceanic crust was involved during the deep burial event associated with a continent–continent collision.

5.1.2. Other major orogens of Gondwana

The ~2500-km-long and ~750-km-wide Damara-Lufilian-Zambezi Orogen was formed by a collision between the Kalahari and Congo-Tanzania Cratons in southern Africa during the late Neoproterozoic. In the Zambezi Belt, central Zambia, phengite- and kyanite-bearing mafic eclogites with garnet-whole-rock Sm–Nd isochron ages of 595 ± 10 and 638 ± 16 Ma have interpreted burial depths of ~90 km (John et al., 2003), and the Lufilian Arc contains whiteschists (talc-kyanite schists) characteristic of granulite-facies metamorphism involving burial to 12–14 kbar

Table 1
 Summary of the age plus maximum pressure and temperature conditions during orogenesis in the principal continent-continent collision zones of Gondwana. The locations of data used in the table (A to S) are shown in Fig. 2. Abbreviations: Met, metamorphism; Max, maximum; Temp, temperature; Press, pressure.

Orogen, sample and location	Age (Ma) of peak met	(Depth) Max Press (kbar)	Max Temp (°C)	Description
<i>Transgondwanan Supermountains (East African–Antarctic Orogen): ~8000 km long and up to 1500 km wide; core of Orogen covers an area of at least 8,000,000 km²</i>				
Kerf-Kabus-Sekerr Suture Sabaloka granulites, Sudan (A)	~620(–700?)	(~30 km) 6–8	600–800	Mafic and pelitic migmatite; ages from SHRIMP U–Pb dating of zircons and monazite; Kröner et al. (1987) and Küster et al. (2008)
<i>Mozambique Belt</i>				
Mafic granulite, Mozambique (B)	557 ± 16	(~55 km) 14–17	857–1041	Garnet-pyroxene-bearing high-pressure mafic granulite; age constrained by SHRIMP U–Pb dating of zircons Engvik et al. (2007)
Eclogite gneiss, Malawi (C)	~530–500	(~65 km) 17–18	66–780	Retrossed garnet-bearing eclogite; SHRIMP U–Pb dating of zircon and garnet-whole-rock Sm–Nd isochron; Ring et al. (2002)
Eclogite, southern India (D)	535 ± 5	19	1010	Garnet-clinopyroxene-omphacite eclogite; ages inferred from U–Pb dating of zircons (Santosh and Sajeve, 2006); Santosh et al. (2009)
Mafic granulite, southern India (D)	535 ± 5	12	980–1010	Garnet-bearing mafic granulite; ages from U–Pb dating of zircons (and monazites) (Santosh and Sajeve, 2006); Santosh et al. (2009)
<i>Dronning Maud Land — Shackleton Ranges</i>				
Eclogite gneiss, Shackleton Range (E)	525 ± 5, 520 ± 14	(60–70 km) 23–25	800–850	Garnet-olivine-bearing ultramafic gneiss; garnet-whole-rock Sm–Nd isochron age; Romer et al., 2009
Eclogite, Dronning Maud Land (F)	~540	(34–41 km) 9–11	687–758	Mafic and metapelitic gneiss; age inferred by variety of zircon- and amphibole-dating methods of other units; Board et al. (2005)
<i>Damara-Lufilian-Zambezi Orogen: ~2500 km long and ~750 km wide; core of orogen covers an area of at least 1,875,000 km²</i>				
Gabbroic eclogite, Zambezi Belt (G)	595 ± 10, 638 ± 1	6 (~90 km) 26–28	720–755	Mafic phengite-bearing (and kyanite-bearing) eclogite; age from garnet-whole-rock Sm–Nd isochron; John et al. (2003)
Whiteschist, Zambezi Belt (H)	531 ± 2	9–11	675–725	Anthophyllite-cordierite-kyanite gneiss and garnet-staurolite-kyanite schist; U–Pb monazite age; John et al. (2004)
Whiteschist, Lufilian Arc (I)	529 ± 2, 531 ± 2	12–14	725–775	Garnet amphibolite and biotite-kyanite-garnet gneiss; U–Pb monazite age; John et al. (2004)
<i>Pinjara Orogen: ~4000 km long and ~750 km wide; core of orogen covers an area of at least 3,000,000 km²</i>				
Granulite paragneiss, Prydz Bay (J)	570–510	10–12	950–1050	Granulite paragneiss; age from U–Pb SHRIMP dating of zircons; Kelsey et al. (2008)
Granulite paragneiss, Prydz Bay (K)	~530	(~25 km) 6	850	Granulite-facies ortho- and paragneiss; ages from U–Pb dating of zircons; Fitzsimons (1996, 1997)
Dredge sample, Naturaliste Plateau (L)	~515	5.5–7.5	700	Felsic orthogneiss; age determined by microprobe chemical dating of monazite; Halpin et al. (2008)
<i>Peternam Orogen: ~1000 km long and ~300 km wide; core of orogen covers an area of at least 300,000 km²</i>				
Eclogite, Musgrave Block (M)	~550	(~40 km) ~12		Eclogite-facies metamorphism in shear zone; garnet-whole-rock Sm–Nd isochron age; Camacho and McDougall (1997)
Granulite, Musgrave Block (N)	~560–520	12–13	700–750	Mylonitized dolerite dykes (now garnet granulite facies); inferred age; Scrimgeour and Close (1999)

<i>Adamastor Orogen: ~400 km long and ~400 km wide; core of orogen covers an area of at least 1,600,000 km²</i>									
Granulite, Ribiera Orogen (N)	590–550	7	~700						Metabasic granulites; inferred age; Heilbron (2004) and Machado et al. (1996); Frimmel and Frank (1998)
<i>Brasilía Orogen: ~400 km long and ~400 km wide; core of orogen covers an area of at least 1,600,000 km²</i>									
Eclogite, Guaxupe Belt (O)	629 ± 14	17.5	660						Garnet clinopyroxenite; garnet-whole-rock Sm–Nd isochron age of nearby granulite; Campos Neto and Caby (1999)
Granulite, Guaxupe Belt (O)	~640	14.4	1040						Mafic garnet-bearing granulite; ages from U–Pb dating of zircons (Basei et al., 1995); Del Lama et al. (2000)
Eclogite, Borborema Province (P)	~650–610	17.3	740–800						Gneissic pyroxene-bearing eclogite; inferred age based on Saraiva dos Santos et al. (2009)
Granulite, Borborema Province (P)	680–610	13.3–16.3	735–1010						Saraiva dos Santos et al. (2009)
<i>Transaharan Orogen: ~2000 km long and up to 800 km wide; core of orogen covers an area of at least 1,600,000 km²</i>									
Mafic eclogite nappes, Mali (Q)	~620	25	690–750						Kyanite-omphacite micaschist; Rb–Sr and garnet-whole-rock Sm–Nd isochron ages; Jahn et al. (2001), Caby et al. (2008)
Granulite nappes, Mali (Q)	~620	14	800–900						Garnet-bearing granulite; age inferred from Rb–Sr and garnet-whole-rock Sm–Nd isochron data; Jahn et al. (2001)
Mafic eclogite, Dahomeyides, Togo (R)	~610	18	600						Garnet-omphacite mafic gneiss in nappes; ages from U–Pb dating of zircons (Atttoh et al. (1991) and Atttoh (1998))
Granulite, Ghana (S)	610 ± 2	14	800–900						Garnet-bearing granulite; ages from U–Pb dating of zircons (Atttoh et al. (1991) and Atttoh (1998))

at ~530 Ma (John et al., 2004). ⁴⁰Ar–³⁹Ar ages of 507.9 ± 2.5 Ma for retrograde hornblende assemblages from the Lufilian Arc rocks indicate that rapid uplift and erosion occurred within a few tens of millions of years after peak granulite-facies metamorphism (Vinyu et al., 1999). The presence of Mesoproterozoic ophiolites in the Zambezi Belt (Johnson and Oliver, 2000, 2004) and the low geothermal gradient of the eclogites (John et al., 2003) are interpreted to represent long-lived and rapid subduction of a relatively large (~1000 km wide) basin of cold oceanic lithosphere prior to continent-continent collision from about 600 and 500 Ma (John et al., 2003).

Meert (2003) suggested that the collision zone between the Kalahari and Congo-Tanzania Cratons (i.e., the Damara-Lufilian-Zambezi Orogen) extended farther along strike to the boundary between India and Antarctica, which he defined as the Kuunga Suture. However, Squire et al. (2006a) pointed out that the rocks in the postulated collision zone between the Indian and Antarctic Cratons do not contain ophiolites or any evidence for arc-related magmatism, and that the boundary zone was locally less than 100 km wide and generally defined by high-strain textures (e.g., McLean et al., 2009). Although we acknowledge that some controversy still exists over the nature of this largely ice-covered boundary, the available data suggests a major (Himalayan-style) mountain range did not exist in the region. However, if Meert (2003) is correct then the large Gondwanan mountain ranges are even more extensive than shown in Fig. 2.

The ~4000-km-long and ~750-km-wide Pinjara Orogen stretched from the western margin of Western Australia's Yilgarn Craton into Antarctica, where ice currently obscures most of its location. In the southern Prydz Bay region, ortho- and paragneisses of the Prydz Complex reached granulite-facies conditions during burial to depths of ~25 km (6 kbar and ~850 °C, Fitzsimons, 1996) at about 550–530 Ma (Fitzsimons, 1997). These rocks were rapidly uplifted from about 515 Ma (Zhao et al., 2003), which is similar to the age of exhumed felsic orthogneiss collected from dredge samples from the Naturaliste Plateau, offshore Western Australia (peak conditions of ~700 °C and ~6.5 kbar at about 515 Ma, Halpin et al., 2008). Rare ultra high-temperature metasedimentary rocks are also present in the Prydz Bay region, which indicate that some rocks were buried to depths in excess of 30 km (10–12 kbar and ~950 °C, Kelsey et al., 2003). Although metamorphic data indicate that the Pinjara Orogen underwent rapid uplift and exhumation from about 550 Ma, controversy remains over whether the region represents a major continent-continent collision zone (e.g., Fitzsimons, 1996; Boger et al., 2001; Collins and Pisarevsky, 2005) or a major intracontinental deformation zone (e.g., Phillips et al., 2006, 2009; Kelsey et al., 2008). The presence of eclogite-facies metamorphism, rapidly exhumed from ~40 km in the 300-km-wide and 1000-km-long Petermann Orogen, central Australia (Camacho and McDougall, 1997), which is universally accepted to have formed in an intracontinental setting (Scrimgeour and Close, 1999), highlights that high metamorphic grades do not always equate to convergent-margin settings (Raimondo et al., 2009). Despite this, a mountain

range must have developed above this orogen from at least 550 Ma, although its height and width may not have been as great as the Transgondwanan Supermountains.

The ~4000-km-long and ~400-km-wide Adamastor Orogen formed between the combined Amazon and Rio de la Plata Cratons of South America and Africa's Congo-Tanzanian and Kalahari Cratons in Africa (Cawood and Buchan, 2007). Although many of the rocks from this orogen are now submerged beneath the Atlantic Ocean, minor on land exposures are preserved in northeastern South America and southeastern Africa. Evidence for this orogen representing continent-continent collision associated with the closure of a late Neoproterozoic ocean basin between the African and South American cratons includes the presence of ~900 Ma rift-related volcanic rocks and the inferred remains of ~800 Ma ophiolites in the Arauaí-West Congo Orogen (Pedrosa-Soares et al., 2001), plus 900–750 Ma rift-related and oceanic magmatism in the Gariép Belt (Frimmel and Frank, 1998). The emplacement of inferred arc-related granites between about 620 and 570 Ma in eastern-most Brazil is considered to represent ocean basin closure in the Arauaí-West Congo Orogen, and granites and granulite facies metamorphic rocks in the Ribiera Orogen record burial to pressures of about 7 kbar and temperatures of about 700 °C between about 590 and 550 Ma (Frimmel and Frank, 1998; Pedrosa-Soares et al., 2001; Heilbron et al., 2004; Cawood and Buchan, 2007). The relatively low metamorphic grades in the orogen (i.e., no known eclogite-facies rocks) and the sparse (and somewhat equivocal) data for closure of a large late Neoproterozoic ocean basin during collision between the African (Congo and Kalahari Cratons) and South American (Rio de la Plata and São Francisco Cratons) components may be due to oblique convergence between them (see Goscombe et al. (2005) and Goscombe and Gray (2008)). This may have restricted the height of the mountain range developed along this orogen.

The sparse and discontinuous exposures of Neoproterozoic rocks along the ~4000-km-long Brasilia Orogen and the ~2000-km-long Transaharan Orogen has created some uncertainty about the nature of collisional events associated with amalgamation of West Gondwana, yet age data suggest peak burial and rapid exhumation occurred at about the same time in both regions. In South America, the Borborema Province contains eclogites (up to 17.3 kbar and 740–800 °C) and granulites (up to 13.3–16.3 kbar and 735–1010 °C) generated between about 650 and 610 Ma (Saraiva dos Santos et al., 2009), which correlate temporally with the eclogites (up to 17.5 kbar and ~660 °C) and granulites (up to 14.4 kbar and 1040 °C) in the Guaxupé Belt that were generated between about 640 and 615 Ma (Basei et al., 1995; Campos Neto and Caby, 1999; Del Lama et al., 2000). These ages and characteristics also match those in the Transaharan Orogen, which include eclogites (18 kbar and ~600 °C) in Togo granulites in Ghana (14 kbar and 800–900 °C) that were formed about 610 Ma (Attoh et al., 1997; Attoh, 1998) as well as eclogites (25 kbar and ~690–750 °C) and granulites (14 kbar and ~800–900 °C) in nappes in Mali (Jahn et al., 2001; Caby et al., 2008). Evidence is also available from these regions

for rapid exhumation soon after peak burial, such as in the Dahomeyides where Ar–Ar isotope correlation ages of hornblendes indicate cooling through 500 °C at about 590–570 Ma (Attoh et al., 1997). Remnants of oceanic crust and/or magmatic arc assemblages are also common (e.g., Caby, 1989; Campos Neto and Caby, 1999; Fonseca et al., 2004; Valeriano et al., 2004; dos Santos et al., 2008), which together with the high- and ultra high-pressure metamorphic rocks support the Brasilia and Transaharan Orogens producing major mountain ranges.

Subduction at the margins of Gondwana also produced long mountain ranges during the final stages of, and immediately following, supercontinent amalgamation. The largest and most important of these mountains were probably associated with the 18,000-km-long Terra Australis Orogen, located along the proto-Pacific margin of Gondwana (Fig. 2, Cawood, 2005). Age data for magmatic, ophiolitic and/or metamorphic rocks that were generated or processed in supra-subduction-zone settings along the Terra Australis Orogen suggest that it was active from about 570 Ma until around 300–230 Ma (Cawood, 2005, and references therein). However, in the context of delivering organic C to the ocean, the relative importance of Terra Australis mountains must be assessed carefully. As we pointed out earlier, mountain ranges associated with subduction zones are generally not as high and are smaller in volume than those involving continent–continent collisions (Hyndman, 2005). In the Lachan Orogen, which is the largest of the belts comprising the Terra Australis Orogen in eastern Australia, high-grade metamorphic rocks are absent and the granites commonly intrude their own volcanic pile (Chappell and Stephens, 1988), suggesting that they were never deeply buried or extensively eroded. This interpretation is consistent with palaeotectonic reconstructions of the late Neoproterozoic to Phanerozoic margin of eastern Australia, which displays marked similarities with the West Pacific today (Crawford et al., 2003) and where large mountain ranges are rare. In contrast, structural and metamorphic data from Antarctica suggest that subduction-related orogeny probably did involve substantial mountain ranges, particularly from about 500 Ma (di Vincenzo et al., 1997; Goodge et al., 2004; Cawood, 2005). Similar mountains probably also existed along the margin of West Gondwana, but the evidence for involvement of a subduction zone in the rocks from this region can only be traced back to about 530 Ma (Cawood, 2005). Nevertheless, the enormous size of the Terra Australis Orogen means the peri-Gondwanan mountain ranges would have made a significant additional contribution of nutrients into the late Neoproterozoic–Paleozoic oceans.

5.1.3. Integration of the Gondwanan orogenic events

Our supermountains hypothesis for the late Neoproterozoic rise in O₂ predicts a temporal correlation with mountain-building events associated with Gondwana's amalgamation. As stated earlier, the greater the volume of the supermountains, the greater mass-flux of nutrients into the oceans, the higher the global rate of sedimentation, and the greater the rate of O₂ production and carbon burial. Testing this prediction requires an integration of the

various orogenic events that contributed to the assembly of Gondwana, many of which overlap in time.

The timing of orogenic events is determined by geochronology and the most robust dating method is U–Pb in zircons. We have therefore used a compilation of U–Pb dates of detrital zircons from Earth's major rivers as a proxy for the integrated global orogenic activity (Fig. 1e). Note that the peaks in U/Pb dates at 650–450 Ma and 350–225 Ma correlate with the formation of Gondwana and Pangea respectively. Significant zircon production, and presumably orogenic activity, started at 650 Ma and peaked between 550 and 525 Ma. The date of 650 Ma agrees with an estimate of 630 Ma by [Cawood \(2005\)](#) for the start of Gondwana amalgamation. 650 Ma also coincides with the start of the rise in O₂, and 530 Ma with a peak in the [Berner \(2006\)](#) atmospheric O₂ curve and with the Cambrian radiation (Fig. 1). There is therefore excellent agreement between the rise in atmospheric O₂ and the increasing orogenic activity as assessed from the U–Pb in detrital zircon (Fig. 1e). In particular our hypothesis predicts an increase in atmospheric O₂ from ~650 Ma to the Cambrian Explosion of life at ~530 Ma, which is consistent with O₂ curve as it is known. We stress, however, that the atmospheric O₂ curve is not well known beyond 420 Ma because it cannot be constrained by the appearance, disappearance and change in abundance of charcoal.

5.2. C content of Gondwanan sedimentary rocks

5.2.1. Sedimentary recycling during erosion of the Gondwanan supermountains

Erosion of igneous material in the Gondwanan supermountains would have produced new sedimentary detritus to add to Earth's global sedimentary mass. The fraction of igneous material in the Gondwanan supermountains is difficult to estimate, but it must have been significant to explain the peak in zircon production during the Pan-African orogeny (Fig. 1f). [Veevers \(2007\)](#) reported ages for numerous Pan-African granites but we are unaware of any attempt to estimate the fraction of granite in the eroded roots of the orogeny. Many of the Pan-African granites have formed by melting older sedimentary rocks ([Borg and DePaolo, 1991](#)) and in this sense erosion of this material is effectively recycling older sediments. However, melting of the crust requires a heat source and the most likely source of that heat is mantle-derived basalt that ponds in the crust and mixes with the crustal melts it produces ([Hawkesworth et al., 1981](#)). Oxygen isotopes (δ¹⁸O) for Pan-African granites vary between 4.5 and 10.5 ([Valley et al., 2005](#)), with samples tending to concentrate toward the mantle end (5.3), showing that there is a significant but variable mantle component in Pan-African granites.

5.2.2. Evidence for C-rich Gondwanan sedimentary rocks

There is abundant evidence that the Ediacaran, Cambrian and Ordovician sedimentary rocks produced by erosion of the Gondwanan supermountains were C-rich. Thick packages of Ediacaran C-rich mudstone are found in northwest Canada, East Greenland, Svalbard, central Australia, throughout north Africa, India, Pakistan and

Siberia ([Halverson and Hurtgen, 2007](#); [Grosjean et al., 2009](#)). In Oman, these rocks represent the oldest-known source material for economically significant oil deposits ([Grosjean et al., 2009](#)). Extensive C-rich Cambro-Ordovician sedimentary rocks are found in Arabia, northern Africa, India, Australia (Delamerian Orogen, Grampians, Stawell Zone, Bendigo Zone, Melbourne Zone, Eastern Lachlan Orogen and Tyennan Orogen), New Zealand, Antarctica, South Africa and South America (northern Patagonia) ([Squire et al., 2006a](#), and references therein).

5.2.3. O₂ production from stored organic C in the Ediacaran-Cambrian-Ordovician sedimentary rocks

The mass of O₂ produced by the burial of organic C and pyrite in the Gondwanan sediments can be calculated from the mass of sediment and the average C and S content of ancient terrigenous sedimentary rocks. The average C content of modern terrigenous sediment rocks is 0.6% and the S content is 0.25% ([Berner, 1982](#)). However, ancient terrigenous successions have an average of 0.9% C and 0.35% S ([Holland, 1978](#)). [Berner \(1982\)](#) attributes this difference to increased erosion due to anthropogenic activity, which he argues leads to dilution of the C and S in modern sedimentary units. We have therefore used the average values of [Holland \(1978\)](#) for ancient sedimentary rocks. Taking 2.5×10^{20} kg as the minimum mass of buried Gondwanan sedimentary ([Squire et al., 2006](#)) successions and 0.9% as its C content, the mass C stored in Ediacaran-Cambrian-Ordovician sedimentary units is at least 2.25×10^{18} Kg. The mass of O₂ released by burying a given mass of C can be calculated from the following reaction, which is assumed to represent photosynthesis:

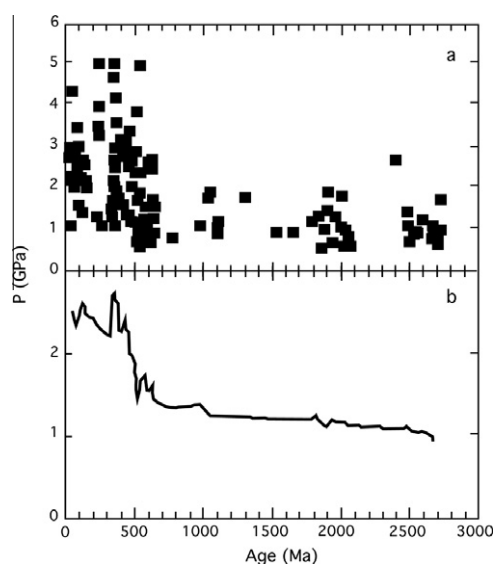
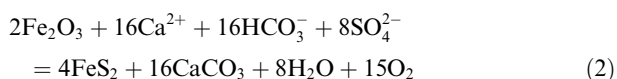


Fig. 3. Peak pressure plotted against age for metamorphic rocks for the global data set of [Brown \(2007\)](#). (a) Individual data points and (b) a nineteen point moving average. Data from [Brown \(2007\)](#) Tables 1–5, plus additional data for samples with ages between 500 and 650 Ma referenced in [Table 1](#).

From Eq. (1) 2.67 kg of O₂ are released for each kg of C sequestered in sedimentary rocks. The mass of O₂ released by burial of C in the Gondwanan sedimentary rocks is therefore 6×10^{18} kg.

The bacterial reduction of seawater sulfate to sulfide, referred to in Section 2, occurs in anoxic terrigenous sediments within a few centimeters to meters of the top of consolidating sediments. Organic C and detrital Fe react with seawater sulfate to produce pyrite plus O₂ and this reaction continues until all of the C or detrital Fe are consumed. The net effect is that organic C, which might otherwise have reduced O₂, instead reduces sulfate to produce O₂. It can be represented by the following equation (Berner and Canfield, 1989)



from which the burial of 1 kg of S releases 1.9 kg of O₂. The mass of O₂ released by burial of pyrite in 2.25×10^{18} kg of sediment containing an average of 0.35% S is 1.5×10^{18} kg and the total mass of O₂ produced by burial of C and pyrite is at least 7.5×10^{18} kg. This is ten times the amount of O₂ ($0.6\text{--}1.0 \times 10^{18}$ kg) required to raise its concentration in the atmosphere from the low levels (say 5% PAL) expected in the early Neoproterozoic to the 60–100% PAL estimated by Berner (2006) and Canfield (2005) for the Cambrian. We suggested that the excess O₂ was consumed by O₂ sinks, especially oxidation of C and pyrite during erosion of the sediments in the Gondwanan Supermountains and the oxidation of reduced volcanic gases, over this period.

6. WHY DID EROSION OF THE GONDWANAN SUPERMOUNTAINS PRODUCE SO MUCH O₂?

The best estimate of the increase in atmospheric O₂ between 650 and 500 Ma is from 5–10% PAL to 60–80% PAL (Canfield, 2005), an increase of at least 50% PAL, which compares with earlier step increases of no more than 5% PAL. If, as we have argued, these step increases are due to the enhanced sediment flux produced by erosion of supermountains following supercontinent amalgamation, the obvious question that must be addressed is why erosion of the Gondwanan supermountains produced an increase in the absolute concentration of atmospheric O₂ that is an order of magnitude greater than those associated with the assembly of earlier supercontinents.

We suggest that erosion of the Gondwanan supermountains produced more free-O₂ than earlier supercontinent amalgamations because the maximum height of the Gondwanan supermountains was greater. Brown (2007) showed that blueschists first appeared in the Neoproterozoic era and became dominant in the Phanerozoic Eon together with lawsonite-bearing blueschists and eclogites, and ultra high-pressure metamorphic rocks. He attributes the sudden appearance of these low geothermal gradient, high-pressure and ultra high-pressure metamorphic rocks to a change from Proterozoic to modern plate tectonics. The change in the pressure of metamorphic rocks with time is illustrated

in Fig. 3. Note that, with the exception of a single point at 2.4 Ga, there is a sharp increase in the maximum pressure of metamorphic rocks from 2 to 5 GPa starting from about 650 Ma (Fig. 3a), and in the average metamorphic pressure from 1.2 to 2.5 GPa (Fig. 3b). Notice also that there is a systematic increase in the average metamorphic pressure from 1.1 to 1.4 GPa between the Late Archean and Neoproterozoic intervals, with a small step between 1.0 and 1.1 Ga, although the latter is based on limited data. We interpret this observation to indicate that there has been a small but systematic increase in the thickness of orogenic belts with time though the Archean and Proterozoic, which may have been followed by a sharp increase of uncertain magnitude in the Late Neoproterozoic.

Caution must be exercised in interpreting the sudden increase in metamorphic pressures at 650 Ma to indicate an increase in the thickness of orogenic belts and therefore mountain heights. The Phanerozoic data is almost certainly biased by over sampling of the high-pressure end-members. Furthermore, outcrops of ultra high-pressure rocks are normally small and the pressures they yield require them to come from depths greater than 90 km, which places them within the mantle, well below the likely base of thickened crust (Yin et al., 2007). They are found in association with subduction zones or continent-continent collisions and are interpreted to be fragments of continental crust that have been dragged into the mantle and returned to the crust in buoyancy driven diapirs (Hall and Kincaid, 2001; Yin et al., 2007) or through channel flow along the subduction zone (Mancktelow, 1995). Furthermore, the ultra-high-pressure rocks in the European Alps formed before the start of the collision between the African and Eurasian plates (Rubatto and Hermann, 2001). As a consequence, the high pressures they record do not imply that they were exposed to high-pressure under a thickened continent and exhumed by erosion of the crustal overburden. High-pressure metamorphic rocks can also be exhumed during extension, which occurs during the gravitational collapse of a convergent orogeny, when the over-thickened crust becomes unstable (Dewey, 1988; England and Molnar, 2005; Lister and Forster, 2009). Although tectonic exhumation reduces the role of erosion in exposing high-pressure metamorphic rocks it does not remove the need for deep burial to produce them and therefore the need for thickened continental crust.

Despite these reservations the correlation between the appearance of high-pressure, low-thermal-gradient metamorphic rocks and GOE-II is intriguing and we suggest that the increase in metamorphic pressure seen in Fig. 3 does correlate with an increase in the height of the mountains that overlay the orogenic belts, although by an amount that is appreciably less than a simplistic interpretation of the data might imply. This conclusion is consistent with appearance of low-thermal-gradient orogenic belts. Cool orogenic zone are stronger and better able to support thickened continental crust and higher mountains before the onset of gravitational collapse.

If the mountains that formed during the amalgamation of Gondwana and Pangea were higher than those that formed during the amalgamation of earlier supercontinents

average relief must also have been greater. As we have pointed out, there is log-linear relationship between relief and organic C burial so that a relatively small increase in average global relief will produce a much larger increase in C sequestration. Furthermore, O₂ production must exceed the threshold required to neutralize O₂ sinks, such as reducing volcanic gasses and the oxidation of organic C and pyrite during weathering. The effectiveness of a given increase in O₂ production in raising atmospheric O₂ therefore depends not only on the magnitude of the increase but also on the extent that the rate of increase exceeds the O₂ sink threshold.

6.1. Other factors

Although we have argued that relief dominated erosion and sedimentation rates in the late Neoproterozoic it is likely that two glaciations, the Marinoan and Gaskiers glaciations at 663–636 and 580 Ma, respectively, also contributed. We agree with Halverson and Hurtgen (2007) that a CO₂-rich post-glacial atmosphere and the mechanical abrasion of continental glaciers would have promoted weathering and erosion respectively and note that the Marinoan Glaciation correlates with the onset for the rise of O₂ at ~650 Ma. However, as we have already pointed out, there is no evidence that the Sturtian Glaciation produced an increase in atmospheric O₂. Furthermore, the glaciations cannot explain the rise in O₂ continuing to about 530 Ma (Fig. 1), 50 Myr after the last glaciation. We therefore suggest that although the Marinoan and Gaskiers glaciations contributed to erosion and sedimentation during the late Neoproterozoic, their influence was second order compared with relief.

Two other factors combine to make the late Neoproterozoic a period of rapid erosion and sedimentation. First, primitive land-based biota, which are capable of breaking down feldspars the glue that binds most igneous rocks together, had evolved in the soils. The erosion of supermountains that formed during the amalgamation of pre-Gondwanan supercontinents would have been slowed by the absence of soil biota. Second, the Transgondwanan Supermountains, the largest mountain range in Gondwana, formed in or close to the monsoon belt (Fig. 2). The short seasons of extreme rainfall associated with monsoons provide ideal conditions for the rapid erosion and sedimentation (Leier et al., 2005) and therefore for the production and burial of organic C.

7. THE RISE OF ATMOSPHERIC O₂ BETWEEN 350 AND 275 MA

We also suggest that the rise of atmospheric O₂ between 350 and 275 Ma was a consequence of erosion of the supermountains produced during the assembly of Pangea. This mountain chain, which was 8000 km long and up to 1000 km wide (Matte, 2001), is similar in size to the Transgondwanan Supermountains and it is interesting to note that the amount of O₂ that must be added to the atmosphere to produce the calculated O₂ increase in the Berner model (Berner, 2006), for both the 350–275 Ma and 650–525 Ma increases, is 9×10^{17} kg. It has been argued that

burial of large amounts of lignite, in the widespread Carboniferous and Permian coal measures, was responsible for the 350–275 Ma increase in O₂ (Berner, 2006). The relative importance of terrestrial or marine sediments as C sinks in the modern Earth is uncertain due principally to the scarcity of relevant data (Stallard, 1998). Field et al. (1998) argue that over 55% of the O₂ production today comes from phytoplankton whereas Dean and Gorham (1998) calculate that only 25% of modern organic C is sequestered in marine sediments, the balance being stored in lakes (10%), reservoirs (40%) and peatlands (25%). If the contribution of man-made reservoirs is ignored the percentage of C stored in marine sediments rises to 40%. However, on a stable continent these figures are largely irrelevant because C storage in terrestrial reservoirs, such as lakes and peatlands, is temporary and will eventually be reworked during denudation, and either oxidized or transported to the oceans.

The situation in an active tectonic region is different. Deformation can lead to the formation of intra continental basins suitable for the accumulation and preservation of large volumes in terrestrial sediments, foreland basins being an example (Catuneanu et al., 2005). The Mid-Pangean Mountains formed close to the equator and resulting high orographic rain would have produced ideal conditions for the growth of tropical rain forests. Furthermore, rapid erosion and high sedimentation rates during this tectonically active period would have provided nutrients to the subsiding coal swamps and ensured that a high fraction of the peat produced was buried so that it could not back react with atmospheric O₂. The importance of terrestrial C sequestration during this period can be assessed from the high C/S ratio of Permo-Carboniferous sediments, which require the sediments to be pyrite-poor, and indicate deposition in a non-marine freshwater or euxinic environment (Berner and Raiswell, 1983). Although lignite burial may have been the dominate form of C sequestration during the Permo-Carboniferous we note that the 650–525 Ma increase in atmospheric O₂, which is comparable in magnitude to the 350–275 Ma increase, was accomplished without lignite burial. Therefore we suggest that phytoplankton also made a significant contribution to the high concentration of O₂ in the Permo-Carboniferous atmosphere, which at its peak may have reached 30% (Fig. 1e).

8. CONCLUSIONS

Divergence of lineages during the Proterozoic, especially the emergence of soil biota during the Mesoproterozoic or Neoproterozoic eras and evolutionary changes in eukaryotic algae, may have prepared the way for the emergence of animals and the Cambrian Explosion (Knoll and Carroll, 1999) but cannot explain these events. A trigger is required. Oxygen, which was critical to the evolution of animals, is the most likely candidate (Canfield et al., 2007). We suggest that high relief over a large area, which resulted from the formation of the Transgondwanan Supermountains, led to a marked increase in the rate of erosion and, as a consequence, to a marked increase in the global flux of sediment into the oceans. The resulting increase in

the supply of essential nutrients into the oceans, especially P and Fe, led to an explosion of primitive plant life in the Gondwanan upper oceans, and to increased photosynthetic activity and O₂ production. The log-linear relationship between relief and C burial suggests that relief is the driving mechanism for C sequestration and that evolutionary factors are of secondary importance. Enhanced C burial between 650 and 530 Ma initially raised atmospheric O₂ to the critical level required for the existence of animals, and later to a higher level that allowed them to flourish and multiply (i.e., the Cambrian Explosion).

ACKNOWLEDGEMENTS

We thank Robert Berner, Jochen Brocks, Ross Griffiths and David Kelsey for their helpful suggestions.

REFERENCES

- Abdelsalam M. G. et al. (2003) Neoproterozoic deformation in the northeastern part of the Saharan metacraton, northern Sudan. *Precambrian Res.* **123**(2–4), 203–221.
- Abdelsalam M. G., Liégeois J.-P. and Stern R. J. (2002) The Saharan metacraton. *J. Afr. Earth Sci.* **34**, 119–136.
- Abdelsalam M. G. et al. (1998) The Neoproterozoic Kerf suture in NE Sudan: sinistral transpression along the Eastern margin of west Gondwana. *J. Geol.* **106**, 133–147.
- Allen P. A. and Etienne J. L. (2008) Sedimentary challenge to Snowball Earth. *Nat. Geosci.* **1**, 817–825.
- Attoh K. (1998) High-pressure granulite facies metamorphism in the Pan-African Dahomeyide Orogen, West Africa. *J. Geol.* **106**, 236–246.
- Attoh K., Dallmeyer R. D. and Affaton P. (1997) Chronology of nappe assembly in the Pan-African Dahomeyide Orogen, West Africa: evidence from ⁴⁰Ar/³⁹Ar mineral ages. *Precambrian Res.* **82**, 153–171.
- Attoh K., Hawkins D., Bowring S. and Allen B. (1991) U-Pb zircon ages of gneisses from the Pan-African Dahomeyide orogen, West Africa. *EOS Trans. Am. Geophys. Union* **72**, 299.
- Basei M. A. S., Siga, Jr., O., Sato K. and Sproesser W. M. (1995) A metodologia Urânio-Chumbo na Universidade e São Paulo, Princípios metodológicos, aplicações e resultados obtidos. *An. Acad. Bras. Cienc.* **67**, 221–237.
- Beerling D. J. et al. (2002) Carbon isotope evidence implying high O₂/CO₂ ratios in the Permo-Carboniferous atmosphere. *Geochim. Cosmochim. Acta* **66**, 3757–3767.
- Bergman N. M., Lenton T. M. and Watson A. J. (2004) Copse: a new model of biogeochemical cycling over Phanerozoic time. *Am. J. Sci.* **304**, 397–437.
- Berkner L. V. and Marshall L. C. (1965) On the origin and rise of oxygen concentration in the Earth's atmosphere. *J. Atmos. Sci.* **22**, 225–261.
- Berner R. A. (1982) Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. *Am. J. Sci.* **282**, 451–473.
- Berner R. A. (2006) GEOCARBSULF: a combined model for Phanerozoic atmospheric O₂ and CO₂. *Geochim. Cosmochim. Acta* **70**, 5653–5664.
- Berner R. A. and Canfield D. E. (1989) A new model for atmospheric oxygen over Phanerozoic time. *Am. J. Sci.* **289**, 333–361.
- Berner R. A. and Raiswell R. (1983) Burial of organic carbon and sulfur in sediments over Phanerozoic times: a new theory. *Geochim. Cosmochim. Acta* **47**, 855–862.
- Berner R. A., VandenBrooks J. M. and Ward P. D. (2007) Oxygen and evolution. *Science* **316**, 557–558.
- Bingen B. et al. (2009) Geochronology of the Precambrian crust in the Mozambique belt in NE Mozambique, and implications for Gondwana assembly. *Precambrian Res.* **170**, 231–255.
- Board W. S., Frimmel H. E. and Armstrong R. (2005) Pan-African tectonism in the western Maud belt: P–T–t path for high-grade gneisses in the H.U. Sverdrupfjella, East Antarctica. *J. Petrol.* **46**, 671–699.
- Boger S. D. and Miller J. M. (2004) Terminal suturing of Gondwana and the onset of the Ross-Delamerian Orogeny: the cause and effect of an early Cambrian reconfiguration of plate motions. *Earth Planet. Sci. Lett.* **219**, 35–48.
- Boger S. D., Wilson C. J. L. and Fanning C. M. (2001) Early Palaeozoic tectonism within the East Antarctic craton: the final suture between east and west Gondwana? *Geology* **29**, 463–466.
- Borg S. G. and DePaolo D. J. (1991) A tectonic model of the Antarctic Gondwana margin with implications for southeastern Australia – isotopic and geochemical evidence. *Tectonophysics* **196**(3–4), 339–358.
- Bristow T. F. and Kennedy M. J. (2008) Carbon isotope excursions and the oxidant budget of the Ediacaran atmosphere and ocean. *Geology* **36**, 863–866.
- Brocks J. J. et al. (2005) Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**, 866–870.
- Broker W. S. (1982) Glacial to interglacial changes in ocean chemistry. *Prog. Oceanogr.* **11**, 151–197.
- Brown M. (2007) Metamorphic conditions in orogenic belts: a record of secular change. *Int. Geol. Rev.* **49**(3), 193–234.
- Butterfield N. J. (2009) Oxygen, animals and ocean ventilation: an alternate view. *Geobiology* **7**, 1–7.
- Butterfield N. J., Knoll A. H. and Swett K. (1990) A bangiophyte red alga from the Proterozoic of arctic Canada. *Science* **250**, 104–107.
- Caby R. (1989) Precambrian terranes of Benin Nigeria and Northeast Brazil and the Late Proterozoic South Atlantic. In *Terranes in the Circum-Atlantic Paleozoic Orogens* (ed. R. D. Dallmeyer). Geological Society of America Special Paper, pp. 145–158.
- Caby R. et al. (2008) Neoproterozoic garnet-glaucophanites and eclogites: new insights for subduction metamorphism of the Gourma fold and thrust belt (eastern Mali). In *The Boundaries of the West African Craton* (eds. N. Ennih and J. P. Liégeois). Geological Society of London, pp. 203–216.
- Camacho A. and McDougall I. (1997) Timing and exhumation of eclogite facies shear zones, Musgrave block, central Australia. *J. Metamor. Geol.* **15**, 735–751.
- Campbell I. H. and Allen C. M. (2008) Formation of supercontinents linked to increases in atmospheric oxygen. *Nat. Geosci.* **1**, 554–558.
- Campos Neto M. and Caby R. (1999) Neoproterozoic high-pressure metamorphism and tectonic constraint from the nappe system south of the São Francisco Craton, southeast Brazil. *Precambrian Res.* **97**, 3–26.
- Canfield D. D., Poulton S. W. and Narbonne G. M. (2007) Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. *Science* **315**, 92–95.
- Canfield D. E. (2005) The early history of atmospheric oxygen: homage to Robert M. Garrels. *Annu. Rev. Earth Planet. Sci.* **33**, 1–36.
- Canfield D. E. et al. (2008) Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. *Science* **321**, 949–952.
- Catuneanu O. et al. (2005) The Karoo basins of south-central Africa. *J. Afr. Earth Sci.* **43**, 211–253.

- Cawood P. A. (2005) Terra Australis Orogen: Rodinia breakup and development of the Pacific and Iapetus margins of Gondwana during the Neoproterozoic and Paleozoic. *Earth Sci. Rev.* **69**, 249–279.
- Cawood P. A. and Buchan C. (2007) Linking accretionary orogenesis with supercontinent assembly. *Earth Sci. Rev.* **82**, 217–256.
- Chappell B. W. and Stephens W. E. (1988) Origin of infracrustal (I-type) granite magmas. *Trans. R. Soc. Edinburgh: Earth Sci.* **79**, 71–86.
- Chen J. Y. and Zhou G.-Q. (1997) Biology of the Chengjiang fauna. *Bull. Natl. Mus. Natl. Sci. (Taichong, Taiwan)* **10**, 11–106.
- Cloud P. E. (1968) Oxygen in the Precambrian atmosphere: an evolution of the geological evidence. *Science* **160**, 729–736.
- Collins A. S. and Pisarevsky S. (2005) Amalgamating eastern Gondwana: the evolution of the circum-Indian orogens. *Earth Sci. Rev.* **71**, 229–270.
- Cook P. J. and Shergold J. H. (1984) Phosphorus, phosphorites and skeletal evolution at the Precambrian–Cambrian boundary. *Nature* **308**, 231–236.
- Crawford A. J., Meffre S., and Symonds P. A. (2003) 120 to 0 Ma tectonic evolution of the southwest Pacific and analogous geological evolution of the 600 to 220 Ma Tasman Fold Belt System. In *Evolution and Dynamics of the Australian Plate* (eds. R. R. Hillis and R. D. Müller). Geological Society of Australia Special Publication 22 and Geological Society of America Special Paper 372, pp. 383–403.
- Cutten H., Johnson S. P. and De Waele B. (2006) Palaeoproterozoic to Neoproterozoic growth and evolution of the eastern Congo Craton: its role in the Rodinia puzzle. *Precambrian Res.* **160**, 127–141.
- Dean W. E. and Gorham E. (1998) Magnitude and significance of carbon burial in lakes, reservoirs and peatlands. *Geology* **26**, 535–538.
- Del Lama E. A., Zanardo A., Oliveira M. A. F. and Morales N. (2000) Exhumation of high-pressure granulites of the Guaxupé complex, southeastern Brazil. *Geol. J.* **35**, 231–249.
- Derry L. A. and France-Lanord L. M. (1996) Neogene growth of the sedimentary organic carbon reservoir: constraints from the isotopic record. *Paleoceanography* **11**, 267–275.
- Derry L. A., Kaufman A. J. and Jacobsen S. B. (1992) Sedimentary cycling and environmental change in the late Proterozoic: evidence from stable and radiogenic isotopes. *Geochim. Cosmochim. Acta* **56**(3), 1317–1329.
- Des Marais D. J., Strauss H., Summons R. E. and Haynes J. M. (1992) Carbon isotope evidence for stepwise oxidation of the Proterozoic environment. *Nature* **359**, 605–609.
- Dewey J. F. (1988) Extensional collapse of orogens. *Tectonics* **7**, 1123–1139.
- di Vincenzo G., Palmeri R., Talarico F., Andriessen P. A. M. and Ricci C. A. (1997) Petrology and geochronology of eclogites from the lanternman range, Antarctica. *J. Petrol.* **38**, 1391–1417.
- dos Santos T. J. S., Fetter A. H., and Neto J. A. N. (eds.) (2008) *Comparisons between the Northwestern Borborema Province, NE Brazil, and the Southwestern Pharusian Dahomey Belt, SW Central Africa. West Gondwana: Pre-Cenozoic Correlations Across the South Atlantic Region*. Special Publication 294. The Geological Society of London, pp. 101–119.
- Dudley R. (1998) Atmospheric oxygen, giant Paleozoic insects and the evolution of aerial locomotor performance. *J. Exp. Biol.* **201**, 1043–1050.
- England P. and Molnar P. (2005) Late quaternary to decadal velocity fields in Asia. *Geophys. Res.* **110**, B12401. doi:10.1029/2004jb003541.
- Engvik A. K. et al. (2007) P–T–t evolution and decompression textures of Pan-African high-pressure granulites, Lurio Belt, northeastern Mozambique. *J. Metamor. Geol.* **25**, 935–952.
- Falkowski P. G. (1997) Evolution of the nitrogen cycle and its influence on the biological sequestration of CO₂ in the ocean. *Nature* **387**(387), 272–275.
- Falkowski P. G. and Isozaki Y. (2008) The story of O₂. *Science* **322**, 540–542.
- Falkowski P. G. et al. (2005) The rise of oxygen over the past 205 million years and the evolution of large placental mammals. *Science* **309**, 2202–2204.
- Falkowski P. G. and Knoll A. H. (2007) *Evolution of Primary Producers in the Sea*. Academic Press, San Diego.
- Farquhar J. and Wing B. A. (2003) Multiple sulfur isotopes and the evolution of the atmosphere. *Earth Planet. Sci. Lett.* **213**, 1–13.
- Field C. B., Behrenfeld M. J., Randerson J. T. and Falkowski P. (1998) Primary production of the biosphere: integrating terrestrial and oceanic components. *Science* **281**, 237–240.
- Fike D. A., Grotzinger J. P., Pratt L. M. and Summons R. E. (2006) Oxidation of the Ediacaran Ocean. *Nature* **444**, 744–747.
- Fitzsimons I. C. W. (1996) Metapelitic migmatites from Brattstrand Bluffs, East Antarctica – metamorphism, melting and exhumation of the mid crust. *J. Petrol.* **37**, 395–414.
- Fitzsimons I. C. W. (1997) The Brattstrand Paragneiss and the Søstrene Orthogneiss: a review of Pan-African metamorphism and Grenvillian relics in southern Prydz Bay. In *The Antarctic Region: Geological Evolution and Processes* (ed. C. A. Ricci). Terra Antarctica Publications, Siena, pp. 121–130.
- Fitzsimons I. C. W., and Hulscher B. (2005). *Out of Africa: detrital zircon provenance of central Madagascar and Neoproterozoic terrane transfer across the Mozambique Ocean*. Terra Nova (17).
- Flowerdew M. J. et al. (2007) Combined U–Pb geochronology and Hf isotopes geochemistry of detrital zircons from early Paleozoic sedimentary rocks, Ellsworth–Whitmore Mountains block, Antarctica. *Geol. Soc. Am. Bull.* **119**, 275–288.
- Fonseca M. A., de Oliverira C. G., and Evangelista H. J. (2004) The Araguaia belt, Brazil: part of a Neoproterozoic continental-scale strike-slip fault system. In *The 750–550 Ma Brasiliano Event of South America* (eds. R. Weinberg, R. A. J. Trouw, R. Fuck and P. Hackspacher). J. Virtual Explorer, Electronic ed., pp. Paper 6, ISSN 1441-8142.
- Frimmel H. E. and Frank W. (1998) Neoproterozoic tectonothermal evolution of the Gariiep Belt and its basement, Namibia and South Africa. *Precambrian Res.* **90**, 1–28.
- Ganopolski A. and Rahmstorf S. (2001) Rapid changes of glacial climate simulated in a coupled climate model. *Nature* **409**, 153–158.
- Goode J. W., Myrow P., Phillips D., Fanning C. M. and Williams I. S. (2004) Siliciclastic record of rapid denudation in response to convergent-margin orogenesis, Ross Orogen, Antarctica. *Spec. Pap. Geol. Soc. Am.* **378**, 105–126.
- Goscombe B. D. and Gray D. R. (2008) Structure and strain variation at mid-crustal levels in a transpressional orogen: a review of Kaoko Belt structure and the character of West Gondwana amalgamation and dispersal. *Gondwana Res.* **13**, 45–85.
- Goscombe B. D., Gray D. R., Armstrong R. A., Foster D. A., and Vogl J. (2005) Event geochronology of the Pan-African Kaoko Belt, Namibia. *Precambrian Res.* **140**, 103.e1–103.e41.
- Graham J. B., Dudley R., Aguilar N. M. and Gans C. (1995) Implications of the late Palaeozoic oxygen pulse for physiology and evolution. *Nature* **375**, 117–120.
- Grosjean E., Love G. D., Stalvies D. A., Fike D. A. and Summons R. E. (2009) Origin of petroleum in the Neoproterozoic–Cambrian South Oman Salt Basin. *Org. Geochem.* **40**, 87–110.

- Hall P. S. and Kincaid C. (2001) Diapiric flow at subduction zones: a recipe for rapid transport. *Science* **292**, 2472–2475.
- Halpin J. A. et al. (2008) Naturaliste plateau, offshore Western Australia: a submarine window into Gondwana assembly and breakup. *Geology* **36**, 807–810.
- Halverson G. P., Hoffman P. F., Schrag D. P., Maloof A. C. and Rice A. H. N. (2005) Toward a Neoproterozoic composite carbon-isotope record. *Geol. Soc. Am. Bull.* **117**, 1181–1207.
- Halverson G. P. and Hurtgen M. T. (2007) Ediacaran growth of the marine sulfate reservoir. *Earth Planet. Sci. Lett.* **263**, 32–44.
- Hauzenberger C. A. et al. (2007) SHRIMP U–Pb and Sm–Nd garnet ages from the granulite-facies basement of SE Kenya: evidence for Neoproterozoic polycyclic assembly of the Mozambique belt. *J. Geol. Soc. Lond.* **164**, 189–201.
- Hawkesworth C. J., Kramers J. D. and Miller R. M. (1981) Old model Nd ages in Namibian Pan-African rocks. *Nature* **289**, 278–282.
- Heckman D. S. et al. (2001) Molecular evidence for the early colonization of land by fungi and plants. *Science* **293**, 1129–1133.
- Heilbron M. et al. (2004) Brasiliano Orogens in Southeast and South Brazil. In *The 750-550 Ma Brasiliano Event of South America* (eds. R. Weinberg, R. A. J. Trouw and R. Fuck). J. Virtual Explorer, Electronic ed., pp. Paper 4, ISSN 1441-8142.
- Higgins J. A. and Schrag D. P. (2003) Aftermath of a snowball Earth. *Geochem. Geophys. Geosyst.* **4**(3). doi:10.1029/2002GC000403.
- Hoffman P. F., Kaufman A. J., Halverson G. P. and Schrag D. P. (1998) A Neoproterozoic snowball earth. *Science* **281**(5381), 1342–1346.
- Holland H. D. (1978) *The Chemistry of the Atmosphere and Oceans*. Wiley Interscience, New York.
- Holland H. D. (2002) Volcanic gases, black smokers, and the great oxidation event. *Geochim. Cosmochim. Acta* **66**, 3811–3826.
- Hurtgen M. A., Arthur M. A. and Halverson G. P. (2005) Neoproterozoic sulfur isotopes, the evolution of microbial sulfur species, and the burial efficiency of sulfide as sedimentary pyrite. *Geology* **33**(1), 41–44.
- Hyndman R. D. (2005) Subduction zone backarc, mobile belts, and orogenic heat. *GSA Today* **15**, 4–10.
- Jacobs J. and Thomas R. J. (2004) Himalayan-type indenter-escape tectonics model for the southern part of the late Neoproterozoic-early Paleozoic East African–Antarctic Orogen. *Geology* **32**(8), 721–724.
- Jahn B., Caby R. and Monie P. (2001) The oldest UHP eclogites of the World: age of UHP metamorphism, nature of protoliths and tectonic implications. *Chem. Geol.* **178**, 143–158.
- John T., Schenk V., Haase K., Scherer E. and Tembo F. (2003) Evidence for a Neoproterozoic ocean in south central Africa from MORB-type geochemical signatures and P–T estimates of Zambian eclogites. *Geology* **31**, 243–246.
- John T., Schenk V., Mezger K. and Tembo F. (2004) Timing and PT evolution of Whiteschist metamorphism in the Lufilian Arc–Zambezi belt Orogen (Zambia): implications for the assembly of Gondwana. *J. Geol.* **112**, 71–90.
- Johnson S. P. and Oliver G. J. H. (2000) Mesoproterozoic oceanic subduction, island-arc formation and the initiation of back-arc spreading in the Kibaran belt of central, southern Africa: evidence from the Ophiolite Terrane, Chewore inliers, northern Zimbabwe. *Precambrian Res.* **103**, 125–146.
- Johnson S. P. and Oliver G. J. H. (2004) Tectonothermal history of the Kaouren Arc, northern Zimbabwe: implications for the tectonic evolution of the Irumide and Zambezi belts of south central Africa. *Precambrian Res.* **130**, 71–97.
- Jones C. E. and Jenkyns H. C. (2001) Seawater strontium isotopes, oceanic anoxic events, and seafloor hydrothermal activity in the Jurassic and Cretaceous. *Am. J. Sci.* **301**, 112–149.
- Kelsey D. E. et al. (2008) Discovery of a Neoproterozoic basin in the Prydz belt in East Antarctica and its implications for Gondwana assembly and ultrahigh temperature metamorphism. *Precambrian Res.* **161**, 355–388.
- Kelsey D. E., White R. W., Powell R., Wilson C. J. L. and Quinn C. D. (2003) New constraints on metamorphism in the Rauer Group, Prydz Bay, east Antarctica. *J. Metamor. Geol.* **21**, 739–759.
- Kennedy M. J., Droser M., Mayer L. M., Pevear D. and Mrofka D. (2006) Late Precambrian oxygenation; inception of the clay mineral factory. *Science* **311**, 1446–1449.
- Kirschvink J. L. (1992) Late Proterozoic low-latitude global glaciation: the snowball earth. In *The Proterozoic Biosphere: A Multidisciplinary Study* (eds. J. W. Schopf and C. Klein). Cambridge University Press, Cambridge, pp. 51–52.
- Knauth L. P. and Kennedy M. J. (2009) The late Precambrian greening of the Earth. *Nature*, 728–732.
- Knoll A. H. (2003) *Life on a Young Planet: The First Three Billion Years of Evolution on Earth*. Princeton University Press, New Jersey, 277 pp.
- Knoll A. H. and Carroll S. B. (1999) The early evolution of animals: emerging views from comparative biology and geology. *Science* **284**, 2129–2137.
- Knoll A. H., Hayes J. M., Kaufman A. J., Swett K. and Lambert I. B. (1986) Secular variations in carbon isotopes ratios from upper Proterozoic successions of Svalbard and east Greenland. *Nature* **321**, 832–838.
- Kröner A., Stern R. J., Dawoud A. S., Compston W. and Reischmann T. (1987) The Pan-African continental margin in NE Africa: evidence from a geochronological study of granulites at Sabaloka, Sudan. *Earth Planet. Sci. Lett.* **85**, 91–104.
- Kump L. R. (2008) The rise of atmospheric oxygen. *Nature* **451**, 277–279.
- Küster D., Liégeois J.-P., Matukov D., Sergeev S. and Lucassen F. (2008) Zircon geochronology and Sr, Nd, Pb isotope geochemistry of granitoids from Bayuda Desert and Sabaloka (Sudan): evidence for a Bayudian event (920–900 Ma) preceding the Pan-African Orogenic cycle (860–590 Ma) at the eastern boundary of the Saharan Metacraton. *Precambrian Res.* **164**, 16–39.
- Le Hir G. et al. (2009) The snowball earth aftermath: exploring the limits of continental weathering processes. *Earth Planet. Sci. Lett.* **277**, 453–463.
- Leier A. L., DeCelles P. G. and Pelletier J. D. (2005) Mountains, monsoons, and megafans. *Geology* **33**(4), 289–292.
- Lindsay J. F. and Brasier M. D. (2002) Did global tectonics drive early biosphere evolution? Carbon isotope record from 2.6 to 1.9 Ga carbonates of Western Australian basins. *Precambrian Res.*, 114 1–34.
- Lister G. and Forster M. (2009) Tectonic mode switches and the nature of orogenesis. *Lithos* **113**, 274–291.
- Logan G. A., Hayes J. M., Hieshima G. B. and Summons R. E. (1995) Terminal Proterozoic reorganization of biogeochemical cycles. *Nature* **376**, 53–56.
- Machado N., Valladares C., Heilbron M. and Valeriano C. (1996) U–Pb geochronology of the central Ribeira belt (Brazil) and implications for the evolution of the Brazilian orogeny. *Precambrian Res.* **79**, 347–361.
- Mancktelow N. S. (1995) Nonlithostatic pressure during sediment subduction and development and exhumation of high-pressure metamorphic rocks. *J. Geophys. Res.* **100**, 571–583.
- Maruyama S. et al. (2009) The dynamics of big mantle wedge, magma factory, and metamorphic-metasomatic factory in subduction zones. *Gondwana Res.* **16**, 414–430.

- Maruyama S., Liou J. G. and Terabayashi M. (1996) Blueschists and eclogites of the world and their exhumation. *Int. Geol. Rev.* **38**, 485–594.
- Matte P. (2001) The Variscan collage and orogeny (480–290 Ma) and the tectonic definition of the Armorica microplate: a review. *Terra Nova* **13**, 122–128.
- McLean M. A. et al. (2009) Basement interpretations from airborne magnetic and gravity data over the Lambert Rift region of east Antarctica. *J. Geophys. Res.* **114**, B06101.
- McLennan S. M. and Taylor S. R. (1982) Geochemical constraints on the growth of the continental crust. *J. Geol.* **90**, 347–361.
- Meert J. G. (2003) A synopsis of events related to the assembly of eastern Gondwana. *Tectonophysics* **362**(1–4), 1–40.
- Nursall J. R. (1959) Oxygen as a prerequisite for the origin of the metazoa. *Nature* **183**, 1170–1171.
- Pave A. R. (2002) Life on land in the Proterozoic: evidence from the Torridonian rocks of northwest Scotland. *Geology* **30**, 811–814.
- 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* **2**, 27–41.
- Pedrosa-Soares A. C., Noce C. M., Wiedemann C. M. and Pinto C. P. (2001) The Araçuaí–West-Congo Orogen in Brazil: an overview of a confined orogen formed during Gondwanaland assembly. *Precambrian Res.* **110**, 307–323.
- Pehrsson S. J. and Jefferson C. (2009) *Riding the Supercontinent Cycle: Paleoproterozoic Basins and Their Metal Endowment*, American Geophysical Union. Geological Association of Canada and Mineralogical Association of Canada Joint Assembly, Toronto, Canada, pp. U74A–U701.
- Pell S. D., Williams I. S. and Chivas A. R. (1997) The use of protolith zircon-age fingerprints in determining the protosource areas for some Australian sand dunes. *Sediment. Geol.* **109**, 233–260.
- Peterson K. J., McPeck M. A. and Evans D. A. D. (2005) Tempo and mode of early animal evolution: inferences from rocks, Hox, and molecular clocks. *Paleobiology* **31**(Suppl. 2), 36–55.
- Phillips G., Wilson C. J. L., Campbell I. H. and Allen C. M. (2006) U–Th–Pb detrital zircon geochronology from the southern Prince Charles mountains, east Antarctica—defining the Archaean to Neoproterozoic Ruker province. *Precambrian Res.* **148**, 292–306.
- Phillips G. N., Kelsey D. E., Corvino A. F. and Dutch R. A. (2009) Continental reworking during overprinting orogenic events, southern Prince Charles Mountains, east Antarctica. *J. Petrol.* **50**, 2017–2041.
- Poulton S. W., Fralick P. W. and Canfield D. E. (2004) The transition to a sulphidic ocean ~1.84 billion years ago. *Nature*, 431 173–177.
- Raimondo T. et al. (2009) Ediacaran intracontinental channel flow. *Geology* **37**, 291–294.
- Ring U., Kröner A., Buchwaldt R., Toulkeridis T. and Layer P. W. (2002) Shear-zone patterns and eclogite-facies metamorphism in the Mozambique belt of northern Malawi, east-central Africa: implications for the assembly of Gondwana. *Precambrian Res.* **116**, 19–56.
- Romer T., Mezger K. and Schmädicke E. (2009) Pan-African eclogite facies metamorphism of ultramafic rocks in the Shackleton range, Antarctica. *J. Metamor. Geol.* **27**, 335–347.
- Rossetti F., Cozzupoli D. and Phillips D. (2008) Compressional reworking of the east African Orogen in the Uluguru mountains of eastern Tanzania at c 550 Ma: implications for the final assembly of Gondwana. *Terra Nova* **20**, 59–67.
- Rubatto D. and Hermann J. (2001) Exhumation as fast as subduction? *Geology* **29**, 3–6.
- Santosh M., Maruyama S. and Sato K. (2009) Anatomy of a Cambrian suture in Gondwana: Pacific-type orogeny in southern India? *Gondwana Res.* **16**, 321–341.
- Santosh M. and Sajeev K. (2006) Anticlockwise evolution of ultrahigh-temperature granulites within continental collision zone in southern India. *Lithos* **92**, 447–464.
- Santosh M., Tsunogae T., Shimizu H. and Dubessy J. (2009) Fluid characteristics of retrogressed eclogites and mafic granulites from the Cambrian Gondwana suture zone in southern India. *Contrib. Mineral. Petrol.* **159**, 349–369.
- Saraiva dos Santos T. J. et al. (2009) Relics of eclogite facies assemblages in the Ceará central domain, NW Borborema province, NE Brazil: implications for the assembly of west Gondwana. *Gondwana Res.* **15**, 454–470.
- Scott A. C. and Glasspool I. J. (2006) The diversification of Paleozoic fire systems and fluctuations in atmospheric oxygen concentration. *Proc. Natl. Acad. Sci. USA* **103**(29), 10861–10865.
- Scott C. et al. (2008) Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* **452**, 456–459.
- Scrimgeour I. and Close D. (1999) Regional high-pressure metamorphism during intracratonic deformation: the Petermann Orogeny, central Australia. *J. Metamor. Geol.* **17**, 557–572.
- Shen Y., Zhang Y. and Hoffman P. F. (2008) On the coevolution of Ediacaran oceans and continents. *Proc. Natl. Acad. Sci. USA* **105**, 7376–7381.
- Shields G. A. and Veizer J. (2002) Precambrian marine carbonate isotope database: version 1.1. *Geochem. Geophys. Geosyst.* **3**(6), 1031.
- Sommer H., Kröner A., Hauzenberger C. and Muhongo S. (2005) Reworking of Archaean and Palaeoproterozoic crust in the Mozambique belt of central Tanzania as documented by SHRIMP zircon geochronology. *J. Afr. Earth Sci.* **43**, 447–463.
- Sperling E. A., Pisani D. and Peterson K. J. (2007) Poriferan paraphyly and its implications for Precambrian palaeobiology. In *The rise and fall of the Ediacaran Biota* (eds P. Vickers-Rich and P. Komarower). Geological Society of London, Special Publication, pp. 355–368.
- Squire R. J., Campbell I. H., Allen C. M. and Wilson C. J. L. (2006a) Did the Transgondwanan supermountain trigger the explosive radiation of animals on Earth? *Earth Planet. Sci. Lett.* **250**, 116–133.
- Squire R. J., Wilson C. J. L., Dugdale L. J., Jupp B. and Kaufman A. L. (2006b) Cambrian back-arc-basin basalt in western Victoria related to evolution of a continent-dipping subduction zone. *Austr. J. Earth Sci.* **53**, 707–719.
- Stallard R. F. (1998) Terrestrial sedimentation and the carbon cycle: coupling weathering and erosion to carbon burial. *Global Biol. Cycles* **12**, 231–257.
- Stein R. (1990) Organic-carbon content sedimentation-rate relationship and its paleoenvironmental significance for marine sediments. *Geo-Marine Lett.* **10**, 37–44.
- Stern R. J. (1994) Arc-assembly and continental collision in the Neoproterozoic east African Orogen; implications for the consolidation of Gondwanaland. *Annu. Rev. Earth Planet. Sci.* **22**, 319–351.
- Turner J. T. (2002) Zooplankton fecal pellets, marine snow and sinking phytoplankton blooms. *Aquat. Microbial Ecol.* **27**, 57–102.
- Urey H. C. (1952) *The Planets: Their Origin and Development*. Yale University Press, New Haven.
- Valeriano C. M. et al. (2004) U–Pb geochronology of the southern Brasília belt (SE Brazil): sedimentary provenance, Neoproterozoic orogeny and assembly of West Gondwana. *Precambrian Res.* **130**, 27–55.

- Valley J. W. et al. (2005) 4.4 billion years of crystal maturation: oxygen isotope ratios of magmatic zircon. *Contrib. Miner. Petrol.* **150**, 561–580.
- Vance D., Bickle M., Ivy-Ochs S. and Kubik P. W. (2003) Erosion and exhumation in the Himalaya from cosmogenic isotope inventories of river sediments. *Earth Planet. Sci. Lett.* **206**, 273–288.
- Vannier J. and Chen J.-Y. (2000) The early Cambrian colonization of pelagic niches exemplified by *Isoxys* (Arthropoda). *Lethaia* **33**, 295–311.
- Veevers J. J. (2003) Pan-African is Pan-Gondwanaland: oblique convergence drives rotation during 650–500 Ma assembly. *Geology* **31**(6), 501–504.
- Veevers J. J. (2007) Pan-Gondwanaland post-collisional extension marked by 650–550 Ma alkaline rocks and carbonatites and related detrital zircons. *Earth Sci. Rev.* **83**, 1–47.
- Vinyu M. L. et al. (1999) $^{40}\text{Ar}/^{39}\text{Ar}$ geochronological constraints on the tectonic evolution of the easternmost part of the Zambezi Orogenic Belt, northeast Zimbabwe. *Precambrian Res.* **98**, 67–82.
- Wang C. Y., Campbell I. H. and Allen C. M. (2009) Rate of growth of the preserved North American continental crust: evidence from Hf and O isotopes in Mississippi detrital zircons. *Geochem. Cosmochim. Acta* **73**, 712–728.
- Yin A. et al. (2007) Early Paleozoic tectonic and thermomechanical evolution of ultrahigh-pressure (UHP) metamorphic rocks in the northern Tibetan plateau, Northwest China. *Int. Geol. Rev.* **49**, 681–716.
- Yuan X., Xiao S. and Taylor T. N. (2005) Lichen-like symbiosis 600 million years ago. *Science* **308**, 1017–1020.
- Zang R. Y., Liou J. G. and Ernst W. G. (2009) The Dabie-Sulu continental collision zone: a comprehensive review. *Gondwana Res.* **16**, 1–26.
- Zeh A., Millar I. L., Kroner U. and Görz I. (1999) The structural and metamorphic evolution of the northern Haskard Highlands, Shackleton range, Antarctica. *Terra Antarct.* **6**, 249–268.
- Zhao Y., Liu X. H., Liu X. C. and Song B. (2003) Pan-African events in Prydz Bay, East Antarctica, and their implications for East Gondwana tectonics. In *Proterozoic East Gondwana: Supercontinent Assembly and Breakup* (eds. M. Yoshida, B. G. Windley and S. Dasgupta). Geological Society, London, Special Publications, London, pp. 231–245.

Associate editor: James Farquhar