The Neoproterozoic carbon cycle

Abstract

The Neoproterozoic Earth system was signiﬁcantly different from the modern world, as evidenced by extraordinary carbon isotope ﬂuctuations that defy conventional explanation. Because Earth’s carbon and oxygen budgets must be balanced on very long time scales (>105 years), such prolonged excursions can best be explained by invoking a vast pool of dissolved organic matter (DOM) in the world’s oceans and its remineralisation by surplus oxidant after pyrite burial. The episodic waxing and waning of a DOM reservoir helps to explain the occurrence and timing of extreme climate events during the Neoproterozoic Era. Ecological dominance by eukaryotes, such as animals and algae, arose from a series of opportunistic radiations of aerobic life forms during periods of net DOM remineralisation and oxygenation.

1. Mass balance

Carbon mass balance Jacques-Joseph Ebelmen may have been the ﬁrst person to picture Earth’s long-term carbon cycle when in 1845 he surmised that all outgassed carbon dioxide, either from volcanoes or oxidative weathering, must eventually be deposited on the seaﬂoor [1]. He correctly concluded that such ‘sedimentary carbon’ could only be released back into the surface environment once an enormous amount of time had passed, following uplift and erosion or metamorphic decarbonation. One of his key insights was to recognise that somewhere in the world, due to locally high temperatures and/or biological mediation, CaCO3 minerals are precipitating from oversaturated seawater. One consequence of this oversaturation, Ebelmen postulated, was that an amount of carbon dioxide precisely equal to the calcium released during silicate weathering will be stored as marine carbonate. In more recent times, the weathering of Mg-silicates has been incorporated into the story [2]. This is partly because dolomite has been a common marine mineral at times and partly because Mg ions tend to exchange with Ca ions during hydrothermal alteration of ocean crust, which therefore constitutes another source of Ca to the ocean. No other cations are considered, at least for the long-term carbon mass balance, because no other major carbonate minerals are close to reaching saturation point in the world’s oceans. The linkage between outgassing, silicate weathering and carbonate deposition (eqn 1) is along with the burial of carbonaceous organic matter, one of the two major CO2 sinks as shown by the celebrated Ebelmen–Urey equation:

CO2 + CaSiO3 = CaCO3 + SiO2  (1)

, which represents the transfer of carbon from the atmosphere to the rock record by a combination of the following two reactions:

2CO2 + 3H2O + CaSiO3 = Ca2+ + 2HCO3- + H4SiO4  (2)

Ca2+ + 2HCO3- = CaCO3 + CO2 + H2O (3)

One major advance over the Ebelmen–Urey analysis came in 1981, when it was argued that the sensitivity of both climate and weathering to atmospheric CO2 could act as a negative feedback, effectively buffering climate against extreme perturbations [3]. Many authors go so far as to state that silicate weathering controls climate, but this overstates the importance of silicate weathering. Long-term climatic trends, such as the persistent cooling over the past 50 million years, require additional long-term forcing and/or positive feedbacks. It is hard to imagine how silicate weathering can both buffer and cause climate change on geological time scales as this would appear to break the ‘Micawber Principle’, named for the colourful character in Charles Dickens’ book David Copperﬁeld. As Micawber discovered to his chagrin, thrift can help to keep you in the black, buffering your bank balance against perturbations, but sustained deﬁcits in your ﬁxed income versus ﬁxed expenditure will inevitably lead one into poverty. It is still a challenge to identify whether sustained changes to the carbon input or output (or both) hold the key to long-term climate forcing. Another important advance was the application of isotope mass balance, which helps us to understand the global carbon cycle via conservation of carbon isotopes. The lever principle tells us that ∼80% of all carbon moving through Earth’s surface reservoirs ends up as carbonate, while ∼20% is removed as organic carbon. In other words, forg =0.2.

*f*org = Forg / (Forg + Fcarb) (4)

This number arises from the following isotope mass balance equations (eqns 5 and 6) when the isotopic composition of carbon input is assumed to be equal to that of the bulk silicate Earth (about −6‰) over time scales greater than those for which carbon sources and sinks can be assumed to be in equilibrium (>105 years). Under such conditions, forg will approximate 0.2 when the long-term average δ13C values for deposited carbonate and organic carbon are 0‰ and −30‰, respectively.

It is a non-trivial task to determine what proportion of total CaCO3 burial derives from Ca–Mg silicate weathering, or even what proportion silicate weathering makes up of the entire net carbon sink, which includes organic carbon burial. This is because (1) rivers today may not be representative analogues for chemical weathering ﬂuxes on geological time scales and (2) riverine Ca and alkalinity (DIC) derive from multiple sources. On time scales longer than the ocean residence time of Ca and Mg, i.e. >106 years, carbonate deposition should equal the Ca+Mg riverine ﬂux. Taking the most widely accepted estimates from inverse modelling [4], ∼13.2% of the global riverine Ca+Mg ﬂux derives from silicate weathering, 4.1% comes from the dissolution of sulfate minerals, while 82.7% can be attributed to the weathering of carbonate minerals. These results are reproduced in more recent studies using updated compilations [5], although a more abstract approach based on the relative solubility of rocks exposed to weathering gave 34:15:51 [6]. If we equate these proportions (13:4:83) with global carbonate burial, they indicate that the net long-term silicate weathering sink is roughly half as large as the organic burial sink. According to some estimates [7], forg is signiﬁcantly lower than 0.2 today, in which case the two sinks might also be of approximately equal size.

13C input = [13C org . *f*org] + [13C carb . (1 – *f*org)] (5)

13C carb = (13C carb-org) . *f*org - 13C input (6)

To understand this problem, let us consider that organic burial increases, possibly due to increased ballast. The reasons for this change are unimportant here but many suggestions Mass balance considerations also help us to interpret long-term trends in the marine carbon isotope record (Figure 1), in which it is difﬁcult to sustain deviations in baseline δ13C values using organic burial alone. To understand this problem, let us consider that increases in organic burial might possibly be due to increased ballast (sinking carbon ﬂux). The reasons for this change are unimportant here, but many suggestions have been made in the literature that are relevant to the Neoproterozoic, e.g. parcelling of organic matter into faecal pellets [8] or larger phytoplankton size [9]. Any such increase in ‘organic production’ would have to be compensated for, on geological time scales, by a lowering of the silicate weathering carbon sink, caused perhaps by a cooler climate. This is because any unilateral increase in organic carbon burial would increase the net carbon sink, thus lowering atmospheric carbon dioxide levels. In the absence of any compensating increase in the net sources of carbon (outgassing or oxidative weathering), the other net sink (silicate weathering) would need to fall in order for net sources and sinks to retain mass balance. Because organic burial depends also on chemical weathering for nutrients, any such re-equilibration would be subject to a strong negative feedback, buffering against extreme deviations in ocean δ13C composition. It seems unlikely that overall Ca ﬂux to the ocean would decrease in tandem with silicate weathering, because evaporite and carbonate minerals are subject to quantitative dissolution and so riverine Ca+Mg ﬂuxes are governed more by physical erosion than by chemical weathering [10–12]. In other words, unlike silicate weathering, the weathering of easily soluble Ca minerals is not directly constrained by the net carbon ﬂux.

Because organic production requires nutrients like phosphorus that are themselves derived from chemical weathering, any sustained increase in organic burial would therefore become self-limiting, reducing any imprint on the long-term carbon isotope record. It was for this reason that Ben Mills and I proposed that times of consistently low δ13C re ﬂect high physical erosion rates, whereby any isotopic response to increased organic burial would be swamped due to the elevated limestone (and evaporite) weathering ﬂuxes [12]. Conversely, we look upon intervals of consistently high δ13C as times of high net carbon ﬂux relative to total or gross carbon throughput, which includes the carbonate weathering ﬂux. To a ﬁrst approximation, therefore, the marine carbon isotope record tells us about the relative importance of chemical and physical weathering, and so is intimately linked to volcanism and tectonic uplift, respectively. Returning to Ebelmen (and many others since), the long-term carbon cycle is usually portrayed as two separate sub-cycles: an inorganic and an organic sub-cycle. Although the carbon mass balance only requires that the two major sources (thermal outgassing and oxidative weathering) balance the two major sinks (silicate weathering and organic burial), these two sub-cycles are commonly assumed to be in equilibrium on geological time scales. This is because oxidative weathering is favoured in Earth’s highly oxygenated surface environment, and so, it may be reasonably assumed that buried organic matter will eventually be oxidised (nearly quantitatively) following exposure to weathering and transport. The same argument can be advanced for pyrite sulﬁde and calcium sulfate, both of which contribute quantitatively to the riverine sulfate ﬂux and have done so since at least 2 billion years. Similarly, limestone weathering and deposition does not result in any net change to the long-term carbon cycle. All these presumed zero-sum relationships greatly simplify the long-term carbon cycle by reducing it to an almost perfect balance between the carbon ﬂuxes associated with thermal outgassing and silicate weathering, but this may be an oversimpliﬁcation. Although sub-cycle balance must prevail over enormous tectonic cycles of uplift and erosion, it does not need to hold true for shorter spans of time (>105–6 to <108 years), for which the complete long-term carbon and oxygen cycles (and carbon isotopes) must still obey mass balance. In other words, the long-term carbon cycle can (and indeed must) be in equilibrium, even when its various sub-cycles are tremendously out of kilter. This has potentially important implications for understanding Earth’s climate and oxygenation history.

2) The DOC reservoir

Average δ13C values decline throughout the Neoproterozoic to Cambrian interval. The trend is consistent with the overall tectonic controls introduced above in so far as it can be interpreted as a sustained decrease in the importance of the net carbon ﬂux (outgassing) relative to the total carbon throughput (=combined outgassing and limestone weathering ﬂuxes). For the Tonian Period, when the denuded supercontinent Rodinia underwent rifting, outgassing would have been compensated for by chemical weathering (coupled to organic burial and carbonate deposition), as per usual, but the contribution of limestone weathering to carbonate deposition would have been lower. Lack of accommodation space due to the persistence of the supercontinent Rodinia may have contributed to the extensive shallow marine limestone platforms and calcium carbonate hypersupersaturation that characterise this period. Decreasing δ13C values through the Neoproterozoic (Figure 1) may therefore relate less to decreasing organic burial or outgassing rates, which were probably rising [13], than to increasing tectonic uplift, erosion and physical weathering, most probably related to the tectonic collisions leading to the formation of Gondwanaland [14,15] by the Cambrian Period. Superimposed on this general decline, the marine carbonate C-isotope record is also characterised by extreme deviations, both positive and negative, from the long-term mean (Figure 2), implying a non-uniformitarian organic sub-cycle [16,17]. The organic sub-cycle is likely to have functioned very differently during the Neoproterozoic. Although the Great Oxidation Event marked the beginning of quantitative oxidation of terrestrial sulﬁde minerals, including pyrite, it seems probable that oxygen levels were still too low to oxidise terrestrial organic carbon to its modern extent. The relatively muted C-isotope record of the middle Proterozoic (the boring billion) may result from this incomplete oxidation because, unlike today, changes to organic burial would have opposing effects on δ13C because any change to forg would be offset by a change to δ13Cinput [18]. Incomplete oxidation of organic carbon would have led to an abundance of detrital organic carbon that would stand less chance of being remineralised in the anoxic and ferruginous Proterozoic sub-surface seawater. As a consequence, much primary and reworked organic matter would have had a long ocean residence time, leading to the build-up of a substantial reservoir of ‘old’ carbon in the world’s oceans. Redox-sensitive elemental and isotopic tracers inform us that the sea ﬂoor was not widely oxygenated until the mid-Ediacaran [19–21], while from organic geochemistry we know that much Proterozoic organic matter was indeed ‘old’ and serially recycled [22]. Following Rothman et al. [16], the negative excursions of the Neoproterozoic are consistent with the episodic oxidation of this vast organic carbon reservoir [16]. Several objections have been made against the ‘DOC oxidation model’ to explain negative carbon isotope excursions [23]. Some authors argue that the anomalies, some of which reach lower values than the canonical (mantle) input value of −6‰, re ﬂect diagenetic alteration [24–26]. Such arguments overlook, however, that the validity of the mass balance principle only depends on whether measured isotopic compositions reﬂect global carbonate deposition. Isotopically depleted limestones and dolostones are ubiquitous in thick, shallow marine successions of late Ediacaran age worldwide [22,27], and so there is no reason to suppose that such low values are unrepresentative of global isotope ﬂuxes. Some base their scepticism on the implausibility of the organic carbon oxidation model, calculating that even were such a huge reservoir to have existed it could not have affected on the carbon isotope record because such large amounts of organic remineralisation would exhaust the available oxidant in the surface environment [24]. Although it is clear that vast amounts of oxidant would indeed be required, sustaining net dissolved organic matter (DOM) oxidation depends not on the size of the available oxidant reservoirs, but on the size of the oxidant ﬂuxes, so this does not seem to be a valid objection. In other words, steady state with respect to oxidant levels can still be maintained if any excess oxygen consumption is balanced by a surplus in oxygen production, in excess of that which is consumed by terrestrial weathering and outgassing sinks. Focusing on oxidant ﬂuxes rather than reservoirs also addresses the objection that the requisite high levels of oxidant could not build up as it would need to be separated physically from the DOC reservoir [23]. A ﬁnal objection is that excess oxidant production through higher organic burial rates would normally be expected to increase forg and therefore δ13C, thus reversing the phenomenon of low δ13C that we are trying to explain [24]. Although a fair comment, oxidant production today derives from both pyrite and organic burial. If, as I presume, the negative excursions reﬂect the sustained transfer over millions of years of ‘old’ organic carbon into the inorganic carbon ocean reservoir, this would cause a decrease in the input value (δ13Cinput) in the carbon isotope mass balance. Normally, this value would be expected to approximate the whole Earth or mantle value, which is assumed to be about −6‰. This number is still likely to be valid during times when the organic carbon reservoir was in dynamic equilibrium or building up. However, for the excursion to be sustained, δ13Cinput would become progressively lower in response to increasing net input of remineralised organic matter towards a new steady state. In many successions worldwide, low values occur consistently through tens to hundreds of metres of carbonate rock. As such thicknesses seem likely to represent several million years, overall steady state with respective to carbon (and carbon isotope) ﬂuxes is an unavoidable assumption even though more organic matter would need to be oxidised than buried for all this time [28]. How is it possible for the Earth system to generate enough oxidant to sustain such imbalance, while maintaining overall balance, in respect to both carbon and oxygen cycles? Currently, almost all the oxidant ﬂux to the surface environment is generated by a combination of organic carbon and pyrite burial, which is assumed to balance the consumption of oxygen by oxidative weathering and degassing. One mole of oxygen is released with every mole of carbon buried, whereas almost double that amount (15/8 moles) is released for every mole of sulfur buried as pyrite. Although this makes bacterial sulfate reduction the more effective oxidant, pyrite formation today is almost everywhere restricted to anoxic pore waters beneath the sea-sediment interface. Pyrite burial links intimately with organic remineralisation and so is favoured in areas of high organic production. However, since the Devonian Period, up to half of all organic burial takes place in terrestrial environments, which are sulfate-poor. Although more than 80% of the modern oxidant ﬂux to the surface environment stems from organic carbon burial today, this seems unlikely to have been the case when organic production was predominantly marine and when oceans were predominantly anoxic. Under such conditions, pyrite burial, the most likely source of surplus oxidant ﬂux, would be favoured, but how much oxidant would need to be generated? During the largest of these excursions, the Shuram anomaly, δ13C values were generally below −8‰, with some distal basinal sections presenting values as low as −15‰ [27]. From eqn (6), and taking representative averages of −10 and −40‰ for buried carbonate and organic matter, respectively, such low sustained δ13C values can be explained by a decrease in (δ13Cinput) from−6 to −13‰, assuming that forg was 0.1, which is a typical value for the Ediacaran–Cambrian transition interval [29]. Taking a suitable value of −30‰ for the old carbon reservoir, the ﬂux of remineralised carbon would need to constitute ∼30% of the total carbon throughput once δInput reached −13‰ at steady state. In other words, the required excess oxidant from pyrite burial would have to be equivalent to about three times the amount released through organic burial. The requirement that net DOM oxidation be sustained for millions of years implies a far larger DOM pool than today’s and far larger even than today’s marine DIC pool [16,28]. Of course, some of the above numbers are used for argument’s sake only, and the real situation may have been slightly different. However, the demonstration is instructive because the suggested values are not only plausible, but deliberately chosen to provide the toughest of tests. If, for example, an equally plausible mean carbonate δ13C value of −8 or−9‰ had been chosen instead, the necessary excess oxidant would have been correspondingly lower and therefore easier to generate. To drive extreme negative excursions, it would appear that the necessary ingredients are high riverine sulfate loads (=high erosion ﬂuxes), high nutrient availability (high chemical weathering ﬂuxes) and largely anoxic, ferruginous oceans, which can turn euxinic at highly productive margins. All these factors are characteristic features of the Ediacaran ocean [30], while due to the enormous carbon ﬂuxes from ocean to atmosphere due to DOM oxidation, eutrophication and euxinia could be self-sustaining due to the resultant global warming and hugely increased chemical weathering ﬂuxes (Figure 3). It seems likely that pyrite burial coupled with DOM oxidation could explain other negative excursions that preceded major glaciations of the Neoproterozoic, too. Indeed, the temporal coincidence between δ13C recovery and the onset of glaciation [31] is consistent with the exhaustion of a DOM reservoir and a diminished capacity for climate buffering [32]. Further elevated organic production and/or pyrite burial rates in the absence of a large DOM reservoir would serve to oxygenate both oceans and atmosphere [28]. Part of the task of the historical Earth scientist is to imagine a world unlike today. The largely anoxic Proterozoic ocean was unlike the modern ocean in that dissolved organic matter was far more abundant. The waxing and waning of this vast but dynamic reductant pool would have acted as a buffer against environmental oxygenation and climatic perturbation, and so its existence is supported by the fact that carbon isotope anomalies precede glacial and oxygenation events. Episodic remineralisation of old marine carbon would also have permitted opportunistic radiations of aerobic organisms, including some of the earliest animal-grade eukaryotes (large Ediacaran benthic fronds and quilts) that must have been suited to the DOM-rich environment. Whether those organisms led osmotrophic lives [33] or directly ingested organic matter, their body plans never subsequently reappeared, suggesting that their life style was uniquely suited to the turbid Ediacaran–Cambrian oceans [34].

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Figure 1. Secular trends in key isotopic parameters in zircons and marine carbonates, modiﬁed from ref. [12]. (C) Magmatic zircon abundances and δ18O values reveal when ﬁve supercontinents formed through orogenic collision (vertical grey bars), leading to greatly increased reworking of sediment during magmatism [35]. (B) The zircon Hf [36] and seawater Sr isotope [37] records anti-correlate, conﬁrming that the Ediacaran–Cambrian interval was a time of exceptional erosional unrooﬁng of crustal roots. (A) The δ13C( forg) minimum at ∼500 Ma [29] occurred during the peak in Gondwanan orogenesis. δ13C( forg) maxima coincide with the existence of Pangea and Rodinia, respectively, before the onset of break-up. The time-averaged δ13C record for the Ediacaran–Present is shown superimposed on a smoothed curve of published data [29].

Figure 2. Cross-calibration of the carbonate carbon isotope, fossil and climate records for the Tonian to Cambrian interval [38,39]. Dark pink bars mark four times of δ13C recovery that directly follow episodic exhaustion of the ocean DOC pool. Three paler blue bars mark glaciations, which follow these negative anomalies [28], whereby the relative timing of the Gaskiers glaciation is less certain.

Figure 3. System analysis diagram [40] showing reservoirs in circles, and ﬂux in square boxes. The arrows indicate a functional dependence of one component on another and its directionality, whereby dashed lines indicate an inverse relationship. Loops with odd numbers of dashed lines represent negative feedbacks. For example, the cooling effect caused by increased chemical weathering (red and green loops) is mitigated here by the positive feedback loop (blue loop) via DOC oxidation (net DOC ﬂux) that restores atmospheric CO2 levels. Likewise, oxygen levels are kept low but stable via the related negative feedback (blue loop), which allows the DOC reservoir to wax and wane in response to ﬂux imbalances.



Figure 1



Figure 2



Figure 3