PALAEOCLIMATE

Slush find

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A coupled model of palaeoclimate and carbon cycling turns up the heat on the idea that Earth once became a giant snowball. It supports instead a milder 'slushball Earth' history — but piquant questions remain.

Sediments laid down in the oceans during the late Neoproterozoic era, between about 850 million and 542 million years ago, tell a dramatic story. They contain wildly varying abundances of the carbon isotope ^{12}C, which is typically incorporated into organic matter during photosynthesis. The pattern of excess ^{12}C in carbonates immediately above and below glacial deposits seems to indicate that photosynthesis on Earth came to a halt during a series of ice ages. These observations are a foundation of the 'snowball Earth' hypothesis[1,2]: that, just before the first appearance of animals, Earth's surface might have been repeatedly frozen over, even at tropical latitudes.

Not necessarily so, say Peltier *et al.* in a recent issue of *Nature*[3]. They apply basic ideas about the solubility of gases to a coupled model of climate and carbon cycling[4] during the frigid late Neoproterozoic era. The results that emerge might explain the oscillatory carbon-isotope compositions of carbonates across the Neoproterozoic glacial cycles, without resorting to the hard-snowball model. Instead, they could lend support to a milder variation on the same theme — 'slushball Earth'.

Figure 1 A soluble solution? The large (5–8-cm high) carbonate crystal fans (black to dark grey), which seem to grow out of the sea floor in this polished slab of a Neoproterozoic 'cap carbonate' from Brazil, suggest the presence of high concentrations of dissolved inorganic carbon in sea water after the ice ages, together with the rapid accumulation of sediments. These fans are draped by grey to white, fine-grained carbonates, which near the top become red, probably because they contain the iron-oxide mineral haematite (Fe_2O_3). The isotopic composition of such geological deposits is a focus of Peltier and colleagues' model interpretation[3] of Neoproterozoic climate and carbon cycling.

The slushball and snowball models both predict ice sheets on continents near the Equator, but with markedly different extents of ice covering the oceans. In the snowball version, the frozen planet is completely blanketed, and reflects most of the Sun's warming rays back into space. Temperatures plummet and surface processes, including life, largely cease. Escape from the snowball state probably requires the build-up of volcanic carbon dioxide in the atmosphere over many millions of years, resulting in torrential acid rain and the intense weathering of exposed rocks during the global thaw.

The slushball model[5], by contrast, predicts open glacial oceans that would have constrained runaway refrigeration by allowing sunlight to warm the planet's surface, driving an active hydrological cycle[6] and photosynthesis[7] in exposed seas. The end of such an ice age need not have required extreme amounts of CO_2 in the atmosphere, nor have been delayed for millions of years.

Peltier and colleagues' new dynamic model[3] shows how climate and atmospheric oxygen might have combined to prevent a runaway snowball Earth. As the oceans cool during ice ages, lower temperatures allow atmospheric gases such as oxygen to diffuse more readily into the deep sea, forcing the oxidation of abundant dissolved organic carbon, formed initially by photosynthesis in surface waters, to CO_2. Released back to the atmosphere by this oceanic 'respiratory' process, the excess CO_2 would warm the planet and thereby end the glacial epoch.

What is particularly interesting about this model is that climate drives the carbon cycle (and so determines the stable levels of atmospheric CO_2). In the most recent ice ages, as well as for earlier interpretations of Neoproterozoic carbon-isotope anomalies[8], the assumption has instead been the other way around. The crucial difference is that the Neoproterozoic carbon cycle was conceivably buffered by a marine pool of dissolved organic carbon that was orders of magnitude larger than that in the present-day oceans[4].

A pertinent criticism of Peltier and colleagues' mathematical model is the uncertainty in its input parameters, in particular the assumption that levels of atmospheric oxygen were similar to those of today (around 21%). Biological[9] and geochemical[10–12] evidence indicates that oxygen levels were low throughout most of the Neoproterozoic, with a significant rise in breathable air around 550 million years ago — about the time animals first appeared on the planet. In that case, it seems likely that pervasive oxygenation of the atmosphere and the hydrosphere, including the vast pool of dissolved organic carbon, occurred millions of years after the extensive ice sheets of the Neoproterozoic had melted away. This rise, known as the Wonoka anomaly after the locality in South Australia in whose rocks it was first observed, is recorded in 550-million-year-old carbonates worldwide that are spectacularly rich in ^{12}C.

The coupled model also does not address certain hallmark geological features of the Neoproterozoic glacial episodes. These include the unexpected appearance of iron-bearing sediments in the glacial deposits, as well as the enigmatic 'cap carbonates' that lie immediately above them (Fig. 1). The co-occurrence of iron-oxide cements and glacial sediments implies that levels of soluble iron increased during the ice age. As iron-bearing minerals such as haematite (Fe_2O_3) are remarkably insoluble in the presence of oxygen, large regions of the ocean must have been largely anoxic during the glacial periods — at odds with the authors' suggestion of progressive oxygenation. A whiff of oxygen would have caused an iron-rich sea to rust, potentially consuming much of the oxidant needed to convert dissolved organic carbon to CO_2. Other potential sinks for oxygen, including weathering of the continents and the oxidation of volcanic gases, were similarly overlooked in the model exercise.

The cap carbonates are testament to the extreme build-up of carbonate anions (alkalinity) in sea water during the Neoproterozoic glacial episodes, and to their wholesale accumulation as carbonate minerals in the glacial aftermath. The oxidative respiration of organic matter produces CO_2 and also creates alkalinity, so Peltier and colleagues' open-ocean solution might also explain the ubiquitous presence of the cap carbonates. But as the authors acknowledge[3], there are other possible oxidants that would work in an anoxic glacial ocean — sulphate, for example[13]. In the absence of free oxygen, sulphate-reducing bacteria could have occupied the water column, as they do in the Black Sea today, and could have fed on the standing pool of organic carbon, progressively raising the concentrations of inorganic carbon. At the same time, their metabolic activity would have released hydrogen sulphide that, when combined with iron, would form the highly insoluble mineral pyrite (FeS_2). The resultant rain of pyrite to the sea floor might help to explain extreme sulphur-isotope variations that are notably present in the post-glacial cap carbonates[14].

These texturally and isotopically distinct carbonates figure prominently in Neoproterozoic palaeoclimate interpretations. In Peltier and colleagues' model, the ^{12}C-rich cap carbonates reflect one stable state of the carbon cycle. But notably, isotopically similar carbonates also accumulated immediately before the ice ages[7,15]. Depending on the timing of CO_2 release, the presence of these deposits can effectively neutralize the authors' proposed solubility hypothesis for the Neoproterozoic ice ages. Not only is more oxygen dissolved when the oceans get colder, so too is more CO_2, which makes water acidic. Acidification of the oceans would have a profound effect on the preservation of carbonate deposited before or after the ice ages.

The variable accumulation of carbonate and iron-oxide-rich deposits across the glacial cycles is not necessarily incompatible with Peltier and colleagues' slushball model[3]. It could well reflect regional differences in seawater salinity and pH, as well as levels of soluble oxygen, sulphate, iron and dissolved organic and inorganic carbon in sea water. The idea of a self-limiting climate as expressed in their model is a tantalizing prospect, and an important contribution to the debate. But our poor understanding of Neoproterozoic ocean dynamics and oxidation add great uncertainty to such mathematical models of Neoproterozoic climate and carbon cycling.

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