Oceanic and atmospheric changes at the end of the Ordovician: geochemical enigmas or the end of a beautiful hypothesis?

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The onset and demise of the end-Ordovician glaciation of Gondwanaland were accompanied by global mass extinction events (Fig. 1). Geochemical studies have revealed changes in ocean circulation and the global carbon cycle that are apparently synchronous with these events. Despite this, the precise relationships between causes and effects and the impact of the events, particularly on the atmosphere, are yet to be resolved. Climate models suggest that atmospheric carbon dioxide levels must have decreased substantially to enable a glaciation in a greenhouse world but geochemical proxy data are equivocal.

Climate change and biotic events

Recent work has indicated that glaciation at the end of the Ordovician was a short-lived event which interrupted a period of long-term greenhouse climate (Brenchley *et al.*, 1994). Direct sedimentological evidence for glaciation comes from a number of localities from Gondwanaland where the duration of the glacial episode has been difficult to determine from terrestrial glacial sequences and glaciomarine deposits. However recent chitinozoan studies have shown that the glacial deposits in North Africa are confined to the Hirnantian, the latest stage of the Ashgill. Sea-level curves from intermediate and low palaeolatitudes also demonstrate a rapid (glacio-) eustatic regression at the start of the Hinantian, and almost as rapid a transgression in the middle of the stage. Both sets of data thus constrain the glacial episode to a very short time period, of probably less than a million years.

Sedimentological and geochemical evidence from deeper water sequences suggest that the glacial period was associated with ventilation of the oceans caused by the onset of thermohaline circulation; grey mudrocks typically replace black shales in such environments. There is some evidence to suggest that the episode of ventilation may have started before the initial regression, at least in some basins.

End-Ordovician mass extinction events appear to be linked, at least temporally, to the climatic and glacioeustatic changes. A first phase of extinction which affected both the plankton and the benthos is closely associated with the base of the Hirnantian. The second phase, associated with the rapid transgression, notably saw the end of the cool-adapted 'Hirnantia fauna' which populated the shelves during the glacial interlude.

The geochemical record

Carbon: Stable isotopic data from marine carbonates and organic matter point to major changes in the global carbon cycle with effects documented from shallow and deep water sediments deposited during the Lower Hirnantian (Marshall *et al.*, 1997). A major positive carbon isotopic excursion of up to 8‰ has been documented from the study of brachiopod calcite and bulk-rock carbonate and/or organics from Europe (Baltic States, Norway and Sweden, and Southern Scotland), North America (Nevada), China and South America. The data thus spans a number of continents and palaeolatitudes and is seemingly global. There is apparently no significant change in the isotopic fractionation between organic and carbonate carbon in the Hirnantian or adjacent stages. Sections from Anticosti Island and the Selwyn Basin in Canada either have a much smaller carbon isotopic shift or apparently record no isotopic excursion which suggests they may be stratigraphically incomplete.

Oxygen: there is evidence for a positive shift in the oxygen isotopic composition of marine carbonates that parallels the carbon shift. This signal is only recorded in the best-preserved brachiopod calcite as the signal from bulk rock carbonates is generally too badly affected by diagenesis. Although the shift is believed to reflect global change in the isotopic composition of carbonate precipitated in equilibrium with sea water the excursion has only been recorded in from the Baltic area (Sweden, Estonia) where the oxygen signal has been preserved because the sediments have never been deeply buried.

Iridium, heavy metals and sulphur isotopes: Despite several studies of the elemental composition of end Ordovician sediments there is no clear picture of global change. Iridium enrichment has been found in sediments close to the Ordovician/Silurian boundary in a number of locations in Canada and in China but there is no evidence that this is associated with bolide impacts: in all instances the anomaly seems to be related to the occurrence of relatively condensed facies where elemental enrichment can be attributed to sea-floor processes rather than to extra-terrestrial supply. Several studies help to elucidate local patterns of environmental change, especially in terms of redox conditions (Berry, *et al.* 1995), but results are not yet widespread enough to demonstrate global patterns.

Implications for the oceans and atmosphere

The shift in oxygen isotopic compositions is relatively simple to explain as a direct result of the glaciation. The shift, of up to 4‰, encountered at low palaeolatitudes, is best explained as a combination of both ice volume and temperature effects. However if the sea level fall (estimated as 100 m) resulted from the accumulation of high latitude ice, the inferred temperature fall in subtropical environments would have been as much as 8°C which seems excessively large in comparison with changes associated with later glaciation.

The carbon isotopic data is even more problematic. The parallel positive shift recorded in organic and inorganic carbon, and from shallow and deep water sites, implies a major shift in global carbon cycling. Conventional interpretation would be that the excursion reflects sequestration of isotopically 'light' organic carbon. As the excursion is more than a transient phenomenon this would imply an increase in the burial (or other removal) of organic carbon rather than merely an increase in productivity. Such removal of carbon is an attractive hypothesis in that it would lead to reduction of aqueous and atmospheric carbon dioxide levels: changes that would be compatible with, or even help to cause, the glaciation. Our published model (Brenchley *et al.*, 1995) indeed suggests that the major growth of ice caps and the extinction events were caused by fundamental changes in ocean circulation nutrient supply and carbon burial. However the model seems to fail in that there is no evidence for the burial of additional carbon in the deep oceans during the early Hirnantian; indeed the sedimentological evidence, as mentioned above, would suggest that the oceans were relatively well ventilated and accordingly that less organic carbon was being buried.

An alternative hypothesis, proposed recently by Lee Kump and colleagues (Kump *et al.* 1997), is that the carbon isotope excursion was caused by a change in the carbon isotopic composition of the total carbon in the oceans. In their model this is driven by a change in the isotopic composition of the riverine input of carbon which is in turn related to a change in global weathering. They argue that a relatively modest increase in the proportion of carbonate weathering, as opposed to silicate weathering, caused by sea-level fall and exposure of late Ordovician epeiric carbonate shelves would be sufficient to give rise to the observed positive excursion. The major drawback to this model is that it needs an independent and earlier set of events to cause the glaciation and substantial sea-level fall prior to the onset of the carbon isotope excursion.

The key to understanding the end Ordovician crises must then lie in the development of an understanding of the precise temporal relationships between changes in oceans and atmosphere. Which came first–the glaciation or the change in carbon cycling? Data from the brachiopod-bearing sections imply synchronous changes but the data are relatively widely spaced at the critical interval. The onset of glaciation in a greenhouse world needs reduced levels of carbon dioxide. Global climate models (Gibbs *et al.*, 1997) indicate that even with favourable continental positioning, the growth of high latitude ice caps would only take place if CO_2 levels were substantially reduced. The isotopic fractionation between organic and inorganic carbon, often used as a proxy for carbon dioxide levels, however remains approximately constant throughout the entire interval. There also little evidence for a sustained decrease in carbon dioxide prior to the beginning of the Hirnantian which would be implicit in Kump *et al*'s weathering model. Alternative models perhaps involving the storage of carbon in ocean basins that are not represented at outcrop today or perhaps in cold ocean water itself are very speculative but may have to be invoked if no other answer can be found!

In summary, then, although biotic and climatic events at the end of the Ordovician are clearly and closely associated with major changes in the global carbon cycle, the driving force(s) for the widespread changes are far from clear.