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Neoproterozoic glass-bleeding

Volcanic eruptions at ocean ridges produce large volumes of glass that is rapidly leached by seawater. Geochemical calculations suggest that this process helps to explain the deposition of carbonates at the end of extreme ice ages.

Ian J. Fairchild

Continental drift over geological time led to the repeated formation and fragmentation of supercontinents. These supercontinents broke up by progressively 'unzipping' along rifts, creating individual continents separated by oceanic crust and a central ridge. These central ridges are shallow, less than two kilometres below the ocean surface, which results in explosive fragmentation of the molten rock as it makes contact with seawater. Chilling leads to glass fragments forming porous bodies of rock called hyaloclastites. The glass is rapidly leached to form a poorly crystalline substance termed palagonite, releasing dissolved calcium, magnesium, silica and phosphorus. Writing in *Nature Geoscience*, Gernon et al.[1] show that the operation of this process during the disintegration of Rodinia between 750 and 650 million years ago could explain the unusual seawater chemistry that occurred during a concurrent and subsequent panglaciation.

During these two episodes of global glaciation, glaciers were globally distributed and reached the coastal margins even at equatorial latitudes. It has been suggested[2] that the Earth experienced a multi-million-year deep freeze caused by a runaway ice-albedo effect during which the oceans were nearly entirely covered in thick ice. Following the end of the glaciations, a cap of carbonate rocks, typically limestone over dolomite, was deposited nearly universally in the shallow oceans. A number of proposals[3] exist for the source of marine carbonate alkalinity, including continental weathering, the deep ocean or iron-reduction. However, it is not clear if they are sufficient, particularly if the carbonates formed in only a few thousand years as in the original Snowball Earth proposal[2].

Gernon et al.[1] argue that a significant source of the alkalinity could lie in the alteration of large amounts of hyaloclastite. In oceans isolated by a thick ice cover, the ions released by submarine weathering of glass would lead to strongly saturated solutions. Simulations by Gernon et al., which allow for various degrees of secondary
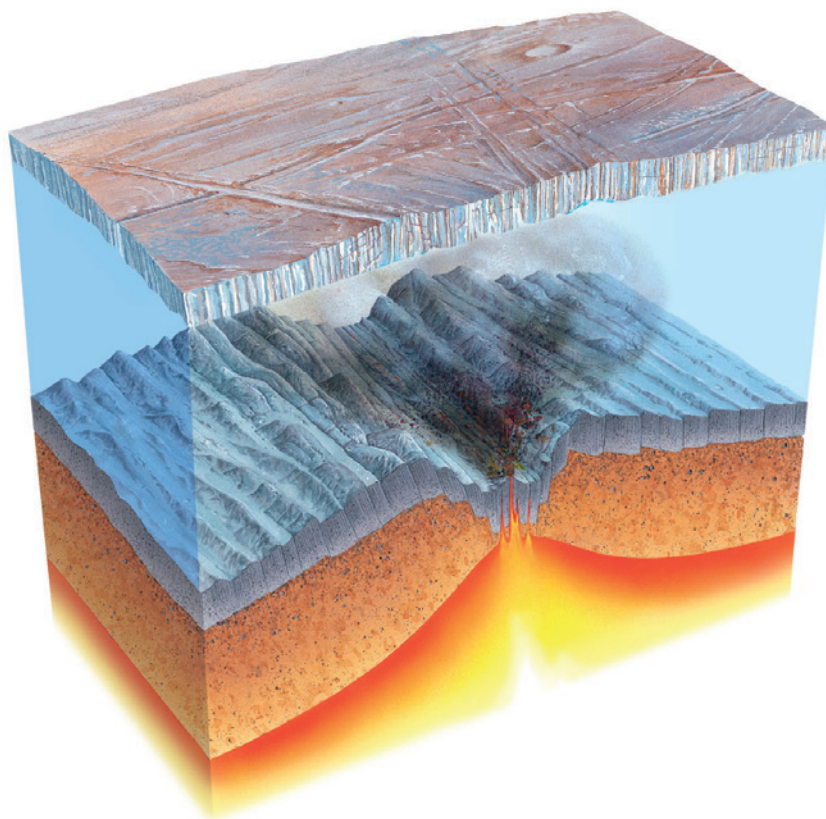

Figure 1 | Shallow ridge effects. The break-up of supercontinents results in explosive submarine volcanism as shallow ocean ridges form and unzip the landmasses. Gernon et al.[1] show that in an ocean with thick ice cover, the leaching of volcanic glass can dramatically alter sub-ice ocean chemistry; their simulated changes reconcile many key features associated with Snowball Earth glaciations. Image by Gary Hincks, reproduced from ref. 1, NPG.

diagenetic cementation of the hyaloclastites, suggest that the glass-leaching mechanism would provide sufficient dissolved species to form at least the dolomite cap over a short time frame. Phosphorus and silica leaching from the glass also explain the presence of siliceous rocks and high P/Fe ratios in iron formations associated with glaciation.

The terrestrial impacts of the fragmentation of Rodinia have previously been identified: greatly increased rainfall and hence chemical weathering in the low latitudes reduced atmospheric carbon dioxide concentrations and set the scene for

global glaciation[4]. A transient increase — over 100 million years or so — in alteration of volcanic glass by seawater removes additional CO_2 from the atmosphere and assists in this process. Continental weathering would also supply phosphorus, even more so if organisms such as lichens had evolved[5]; thus glass-sourced phosphorus was probably most important under Snowball Earth conditions, when weathering products from the continents did not reach the oceans.

Gernon and co-workers' hyaloclastite-leaching concept is framed in terms of a

thick ice cover on the oceans as invoked by the so-called Hard Snowball model (Fig. 1), but other climate model solutions for the Snowball Earth glaciations permit the existence of much larger areas of open water. Indeed, there is evidence for periodic ice-free areas in the ocean during the first and longest glaciation, the Sturtian, whereas the second, Marinoan, global glaciation was probably characterized by more persistent ice cover[6]. Even with an extensive ice cover, sufficient open water would exist to permit exchange of CO_2 between atmosphere and oceans[7].

The release of CO_2 from continued volcanism on land and limited terrestrial weathering under the ice cover permitted atmospheric CO_2 concentrations to increase to high levels. This CO_2 entered the oceans, creating a ready supply available to react with glass[1] or cold igneous rocks[7] on the deep-sea floor. However, Gernon et al. envisage that under thick sea ice, the oceans became strongly supersaturated with carbonate minerals, due to a lack of removal of CO_2 by photosynthesis or a lack of nuclei to aid carbonate precipitation. Their simulations support the idea that oceans were indeed carbonate-saturated, but we lack any direct evidence for either the presence or absence of such carbonate deposits at the peak of glaciation: at this time, carbonates would have been deposited far from the continents, not least because of the kilometre-scale fall in sea level evinced for the Marinoan[8], which would expose not only the carbonate platforms surrounding the continents, but also the

youngest parts of the ocean crust. However, in the later stages of glaciation, carbonate nuclei in the form of carbonate rock flour, produced by the erosion of the carbonate platform by glaciers, were introduced to the oceans through dynamic ice movement. We do have evidence that the nuclei spurred the carbonate precipitation that is recorded in the fine matrix of Sturtian glacimarine deposits[3].

Such deposits are also associated with iron-enrichment, including the local deposition of banded iron formations. These formations are also rich in phosphorus, which could plausibly be sourced from the hyaloclastites. However, in the absence of proxies outside of iron formations for levels of phosphorus, its evolution in the post-glacial ocean remains speculative.

An excursion in the carbon isotopic composition of the cap carbonates towards mantle values suggests a volcanic source for the carbon, such as ridge volcanism, that built up in the oceans and was only minimally cycled, such as by biogenic carbon fixation. A lack of carbon fixation is consistent with the original Snowball Earth model[2], which calls for substantial ice cover and minimal photosynthetic activity. However, protists, and photosynthesizing prokaryotes and eukaryotes nevertheless survived glaciation[9], implying that at least some productivity must have occurred. Of course, the cap carbonates may have formed more slowly than currently envisaged, for instance over hundreds of thousands to millions of years[3]. Such a prolonged

duration of deposition could occur if the meltback of the Snowball Earth glaciation was more gradual than thought: for instance, if the margins of the continental ice sheet terminated inland as proposed by some simulations[6], deglaciation would occur more slowly. In this case, weathered materials from continents may well have also fuelled the carbonate deposition.

Gernon et al.[1] show that the leaching of hyaloclastite glasses on shallow ridges could have dramatically altered ocean chemistry during Snowball Earth glaciations, and fuelled the deposition of massive carbonates. The importance of this process with regards to other sources of alkalinity remains to be determined. ❐

Ian J. Fairchild is in the School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK.
e-mail: i.j.fairchild@bham.ac.uk

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