Neoproterozoic ‘snowball earth’ and the ‘cap’ carbonate controversy

A. V. Sankaran

During the Proterozoic era (2440–540 m.y. ago), the earth went through at least five ice ages[1,2] and among them, the last one that occurred over the late Neoproterozoic (~ 900–540 m.y. ago) is believed to have engulfed the entire earth under ice to create what came to be described as ‘snowball earth’[3,4]. This incredible scenario had stirred up considerable debate among earth scientists, as they wondered how ice could have covered the land masses, which at that time were clustered around earth’s low latitude or the equatorial zone, and also how the planet finally came out of such an icy grip. The Russian climatologist, Mikhail Budyko, explained the possibility for such a snow cover through what is known as ice-albedo feedback or the power of white ice to reflect back solar energy, resulting in progressive cooling of the earth and ice formation. This albedo will be greater in the regions below 30° latitude, where earth’s surface area per degree of latitude is large. This effect, especially under the less bright early-earth sun (~ 25% less than the present-day sun), will induce rapid cooling and promote ice formation gradually over the entire surface of the earth[5,6]. An alternate theory attributes early earth’s high obliquity or tilt (> 54° compared to the current 23.5°), which will make the equatorial zone the coldest place and promote glaciation, though this could not have created a snowball earth[7,8].

After nearly three decades of dormancy since Neoproterozoic global glaciation was first proposed[9], the geological impact of such an ice cover was recognized only in the late 1990s through studies in Namibia carried out by Hoffman and colleagues (Harvard University) and Kaufman (University of Maryland)[10]. Namibia, at this geological time, formed part of the land mass that was drifting from 12°S latitude, further southwards over the next 200 m.y. The team found in the marine carbonates capping the Neoproterozoic glacial deposits (hence called ‘cap’ carbonates) here certain variations in the normal proportions of carbon isotopes. They ascribed these variations to the ups and downs in the CO_2-dependent marine life population when the oceans were in and out of ice cover during this period. Such carbonates succeeding glacial deposits, form an important stratigraphic horizon of Precambrians in a number of countries and they have been investigated in the light of the ice ages this period went through. In India, glaciogenic beds suspected to be products of Proterozoic ice ages have been described and a carbonate bed from Udaipur region of Aravalli Mountain belt registered ^{13}C enrichment related to organic carbon burial (see Box 1).

Some geologists and climatologists were not convinced about the hypothesis of global coverage of ice, including the oceans implicit in the model proposed by Hoffman’s group, as they felt that such an earth could not have ever recovered thereafter. In response to this, Hoffman *et al.*[10] argued that during the millions of years (4–30) that the earth remained under ice, silicate weathering will have ceased and, in turn, this would have arrested the air–sea exchange of CO_2 pouring out of the volcanoes and allowed its build-up in the atmosphere to levels of severe greenhouse conditions. The resultant global warming will boost temperatures (even up to 50°C in the tropics) and lead to rapid melting of the ice within a few decades and liberation of the earth from the ice cover. The atmosphere during this transition to the interglacial period is expected to be hot and steamy, initiating torrential spells of carbonic acid-rich rains that will chemically weather the silicate and other rocks to restore the exchange of CO_2 to the seas. With the advent of warm sea conditions, not only will precipitation of post-glacial marine carbonates resume, but also its biosphere will re-emerge.

The view of Hoffman *et al.*[10] about the impact of glacial and interglacial cycles over the C-isotopes in the carbonates is based on the ability of the CO_2-dependent photosynthesizing marine organisms to offset the normal ratio in these isotopes. These organisms which use CO_2 for their metabolism, preferentially take up the lighter ^{12}C of the two isotopes – ^{12}C and ^{13}C which are present in CO_2 normally at 99% and 1% respectively, (e.g. volcanic emanations) – leaving ^{13}C to get enriched in the waters. Therefore, the carbonates precipitating out of sea water, when these life forms were abundant is expected to show an enrichment of the heavier ^{13}C. In Namibia, it was

Box 1. Proterozoic glacial deposits in India

Even though India formed part of the Neoproterozoic low-latitude continental assembly subjected to the ice cover, surviving evidences for it in this country are scarce. The few glaciogenic tillites, diamictites and boulder beds reported from this period[24], occurring in the Son and Ken Valleys of Madhya Pradesh in the Lower Vindhyan Formations, were initially thought to be products of late Proterozoic ice-age glaciers. But they were later assigned an older Palaeoproterozoic age, on the basis of geochronology[25]. A ~ 50 m thick tillite bed from this locality, the Gangau Tillite, long thought to be glaciogenic, is succeeded by a bed of post-glacial limestone. However, the transition to this limestone bed is not abrupt, which is characteristic of glacial bed/limestone successions. Palaeomagnetic, sedimentological and geochemical studies on the Gangau Tillite bed carried out in 1996, indicated that this bed is not glaciogenic but merely continental debris-flow generated from ferruginous regolith and deposited over 44.7° mid-latitudes[26]. Recently, Sreenivas *et al.*[27] studied carbonate rocks of Jhamarkotra formations, Udaipur region (Aravalli Mountain belt), belonging to the ~ 2200–1900 m.y. period and found ^{13}C enrichment in them. Their studies have ruled out the ^{13}C enrichment arising from local causes or methanogenesis or evaporite conditions. Instead, they found it to be related to high sedimentation rates and rich organic carbon burial. They consider these carbonates as the Indian example of the global ^{13}C excursion during Proterozoic.

observed that ^{13}C in the carbonates just before glacial deposits dropped to standard levels as in volcanic CO_2 emissions and remained at this level up to the cap carbonates, immediately overlying the glacial deposits. Thereafter, it gradually increased to higher levels in the relatively younger cap carbonates laid several metres higher up in the succession. They attribute the drop of ^{13}C just before glaciation to the onset of frigid conditions detrimental to the survival of ^{12}C-preferring marine life. Once the earth started emerging from the ice cover, marine life resurrected and C-isotope levels in the post-glacial carbonates started registering gradual enrichment of ^{13}C.

Even though these explanations appeared plausible, critics were not sure whether oceans with their higher heat potential could ever freeze and, secondly, if the earth can be completely engulfed by ice in view of likely high levels of CO_2 this will build up in the atmosphere[11,12]. To understand the role of oceans, land masses and atmospheric CO_2 under conditions of reduced solar luminosity in the production of global glaciation, a few climatologists conducted studies using different models of palaeogeographic configuration covering earth's high to low latitudes with varying extent of land fractions, topographies, ocean and atmospheric constitution[13,14]. They found that maximum ice cover could extend only up to ~ 55° latitude with a tropical supercontinent configuration. Also, ocean-freeze in the low-latitude region is unlikely (except perhaps in certain isolated sites[15]), in spite of the reduced solar luminosity and low atmospheric CO_2 of the period, mainly due to thermal inertia of the oceans.

The views of climatologists disputing the frozen-ocean scenario are strengthened by the recent find of closely spaced layers of glacial debris within Neoproterozoic glaciomarine successions in Congo, Kalahari and other cratons in Africa[16]. This would indicate that they were downloaded from the glaciers upon their reaching the seas, implying thereby that the seas during those times must have remained ice-free, at least for part of the year. Evidently, the marine life could not have been affected to influence the cap carbonate C-isotope proportions, as reported by Hoffman *et al.*[10]. Further, such massive cap carbonates, as described by this group, would require post-glacial weathering rates ~ 1000 times pre-glacial levels, which is not supported either by calculations of maximum possible weathering rates, or justified by any enhancement of $^{87}Sr/^{86}Sr$ ratio expected in the post-glacial marine sediments over those of pre-glacial deposits[2,15].

Recently, a methanogenic route to the problem of cap carbonate was proposed by Kennedy (University of California), Christie-Blick and Linda Sohl (Columbia University)[17]. According to them, decomposition of the immense mass of trapped organic life on lands under Neoproterozoic ice cover generated methane which remained locked up as permafrost methane hydrate (see Box 2). Rapid melting of ice cover, following the global rise in temperature during post-glacial greenhouse conditions, led to marine transgression (sea-level rise) and submergence of the lands under permafrost. This destabilized the methane hydrates liberating methane, which, being biogenic, will be enriched in ^{12}C. The post-glacial cap carbonates, therefore, show corresponding enrichment in this isotope. Kennedy *et al.*[17] cite a number of indirect features produced by the buoyant cold methane, most of which are also seen in modern seep-sediments. Among these are the seep-related tubular passages, which are believed to have served as home for chemosynthetic organisms. Other features are the disrupted, domed and cracked sediment layers, the cracks often infilled subsequently by marine cements. The authors claim that their methanogenic route is viable, as indicated by good agreement between mass balance estimate of carbon released from destabilized methane hydrates and carbon buried in cap carbonates.

The methane hydrate model has also raised a spate of questions[18,19]. Critics feel that such fossil hydrocarbon-carbonates are usually small features associated with faults or around destabilizing gas unlike the extensive cap carbonates reported, which result from catastrophic destabilization of the methane hydrates disturbing the entire seabed and not through cold methane seeps which Kennedy *et al.*[17] have described. Secondly, neither the variations of the carbon isotope in terms of global ocean history nor the source for immense methane involved is compatible with these carbonates. Also, they suspect that the reported tube-like structures which are not seen in other cap carbonates in the same area may as well be annelid or mollusc fossil remains or simply sedimentation features often present in dolomite beds[18,19]. The absence of bitumen in the carbonates and the depleted levels of ^{13}C in the marine cements filling the cracks are other anomalies, according to the critics, not favouring the methanogenic model[18] In their rebuttal, Kennedy and colleagues[20] state that the methane gas was derived from the decomposition of sizeable mass of accumulated organic matter under permafrost ice whose terrestrial abundance during Neoproterozoic times was much greater than in any other geologic period. They claim that such permafrost methane hydrates usually lack bitumen and assert that the gas was

Box 2. Permafrost methane hydrate

Methane is gaseous at room temperature and atmospheric pressure, but under high pressure (> 50 atm) and low temperature (< 7°C), it combines with water molecules to form an icy-white compound called methane hydrate. In nature, such high-pressure and low-temperature conditions are prevalent in areas of permafrost (permanently frozen ice and soil occurring in very cold regions, both offshore and onshore) and ~ 300–2000 m beneath sea-floors on the outer continental margins and shelves. A modern example of continental permafrost type is present in Alaska as working gas field. Methane hydrate gets destabilized into the gas phase when the pressure decreases or temperature increases from the optimum; for example, when permafrost ice melts or in the case of oceanic types, when the methane hydrate zone extends to greater depths where temperature gets to be higher. The origin of methane gas is not clearly known, though it is believed to be essentially due to microbial reduction of CO_2 derived from organic matter that got buried along with sediments in many sedimentary basins. This view is supported by molecular composition of the hydrocarbon gases and isotopic composition ($\delta\ ^{13}C$) of methane.

released slowly over thousands of years, disturbing the seabed just adjacent to the seepage site. As for the tube-like structures are concerned, they are undoubtedly seep-related and cannot be equated to fossil remains, which are not expected in Neoproterozoic examples.

The late Neoproterozoic glaciation and associated carbonates have been generating a fresh controversy just when the earlier one is about to be settled. Now, the newly proposed 'methane hydrate' model opposing the 'snowball earth' model, which is quite popular among earth scientists, has kept alive the unending debate. The abundance of methane in early earth atmosphere, both volcanogenic and biogenic, is well-documented[21–23]. Its role not only in cap carbonate genesis, but also as an effective greenhouse gas in addition to CO_2 to inhibit ocean-freeze, a vital requirement for the 'snowball earth' model, seems to favour the methane–cap carbonate link. Unless more data from similar carbonates formed during younger-period ice ages become available, an answer to which one of these two routes is likely to have had a part in the genesis of cap carbonate, will have to wait.

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A. V. Sankaran lives at No. 10, P and T Colony, I Cross, II Block, RT Nagar, Bangalore 560 032, India.
e-mail: sankaran@bgl.vsnl.net.in

COMMENTARY

The future of scholarly publishing

John Willinsky

The academic journal has been the mainstay of scholarly publishing for some 350 years, with its current crop of articles bound and printed, issued periodically and serially, from weekly to annually. The journal's print run will continue for some time, it seems certain, but just as certainly, the journal is moving on-line with a rapidity and thoroughness that suggest that this where its future lies, in a way that is not at all so apparent for the scholarly book or any book, for that matter. In the course of the World Wide Web's first decade, at the close of the twentieth century, it has been estimated that some 75% of academic journals are offering some form of on-line access with more than a 1000 peer-reviewed journals publishing only on-line. This immediate, hyperlinked, multimedia environment appears to serve the journal well.

Although much of this shift in publishing mediums amounts to old-wine-in-new-bottles, one radical variation has emerged in the economics of this knowledge. While most journals simply stayed with their subscription model in the great on-line migration of the 1990s, many experimented with free on-line access on first going electronic. That utopian moment soon passed, and on-line editions were restricted to subscribers, and prices rose for print-plus-on-line-access subscriptions, while revenue innovations, such as pay-per-view and site licensing were introduced.

Yet, from the beginning of the Internet, many of those involved in scholarly publishing – and which researcher or faculty member is not in some way – could not help but notice the ease with