

LETTERS

Snowball Earth termination by destabilization of equatorial permafrost methane clathrate

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The start of the Ediacaran period is defined by one of the most severe climate change events recorded in Earth history—the recovery from the Marinoan ‘snowball’ ice age, ~635 Myr ago (ref. 1). Marinoan glacial-marine deposits occur at equatorial palaeolatitudes², and are sharply overlain by a thin interval of carbonate that preserves marine carbon and sulphur isotopic excursions of about –5 and +15 parts per thousand, respectively^{3–5}; these deposits are thought to record widespread oceanic carbonate precipitation during postglacial sea level rise^{1,3,4}. This abrupt transition records a climate system in profound disequilibrium^{3,6} and contrasts sharply with the cyclical stratigraphic signal imparted by the balanced feedbacks modulating Phanerozoic deglaciation. Hypotheses accounting for the abruptness of deglaciation include ice albedo feedback³, deep-ocean out-gassing during post-glacial oceanic overturn⁷ or methane hydrate destabilization^{8–10}. Here we report the broadest range of oxygen isotope values yet measured in marine sediments (–25‰ to +12‰) in methane seeps in Marinoan deglacial sediments underlying the cap carbonate. This range of values is likely to be the result of mixing between ice-sheet-derived meteoric waters and clathrate-derived fluids during the flushing and destabilization of a clathrate field by glacial meltwater. The equatorial palaeolatitude implies a highly volatile shelf permafrost pool that is an order of magnitude larger than that of the present day. A pool of this size could have provided a massive biogeochemical feedback capable of triggering deglaciation and accounting for the global postglacial marine carbon and sulphur isotopic excursions, abrupt unidirectional warming, cap carbonate deposition, and a marine oxygen crisis. Our findings suggest that methane released from low-latitude permafrost clathrates therefore acted as a trigger and/or strong positive feedback for deglaciation and warming. Methane hydrate destabilization is increasingly suspected as an important positive feedback to climate change^{11–13} that coincides with critical boundaries in the geological record^{14,15} and may represent one particularly important mechanism active during conditions of strong climate forcing.

Authigenic carbonates within the Reynella Member of the glacial Elatina Formation occur in coastal cliff exposures of the Marinoan type section in South Australia (Fig. 1 a–d) and provide constraints on the magnitude and timing of methane influence during deglaciation. The Reynella Member is part of a transgressive littoral succession that deepens into the shelfal deposits of the Seaciff sandstone and interbedded cap carbonate of the Nuccaleena Formation¹⁶ (Fig. 1f). The Nuccaleena Formation is the Marinoan cap carbonate that houses the global stratotype section and point for the Ediacaran period, and is widely believed to provide a global tie point shared by the integrated sea level rise driven by global deglaciation⁴. On the basis of the low palaeolatitude², minimal glacial evidence and transgressive sediments, we interpret deposition of the Reynella siltstone

to coincide with local ice withdrawal preceding global eustatic rise recorded by the Nuccaleena Formation (Fig. 1f).

These carbonates form an irregular plumbing system containing sub-vertical chimneys 1–2 m in diameter and branching pipes (Fig. 1a) that coalesce into hard grounds. Microcrystalline dolomite and calcite cement fills pores in sandstone and forms up to 60% of the sediment, indicating precipitation before compaction. In plan view, spar-filled tubes are concentrated within the cores of 1-m-diameter chimneys ringed by cemented sandstone. Morphologies include microcrystalline pore-filling calcite and Fe-rich dolomite with pyrite crystals >10 µm indicative of sulphate reduction, acicular cements (formerly aragonite) fringing synsedimentary breccia clasts of carbonate-cemented sandstone, spar-lined vugs and tubes with Mn-cement coatings, sparry calcite-filled veins often forming a honeycomb crust morphology, and isolated centimetre-scale bladed crystal fans of calcite pseudomorphs after barite. Calcite spar is present in early veins, thin vertical tubes and vugs, and within hard grounds. Both dolomite and calcite cements and calcite spar comprise clasts eroded and reworked by currents within channelized, cross-bedded sand and breccia deposits (Fig. 1b). These indicate a dynamic system, including erosion with re-cementation in shallow seafloor sediments rather than a more typical history of cementation during burial. Breccias of similar composition occur as metre-scale, massive, vertically oriented cross-cutting fluidized beds (Fig. 1c, d) that erupted on the sea floor and were reworked by seafloor currents into cross-bedded channel-fill. Sedimentary features indicative of vertical fluid or gas migration, overpressure, seafloor reworking and complex seafloor paragenesis are diagnostic of a methane cold-seep origin^{17,18}. This complex morphology contrasts with the regionally extensive laminated dolomicrite of the overlying Nuccaleena Formation and the sparry calcite that fills cross-cutting fractures aligned with regional folding.

Authigenic cements within these morphologies show the broadest range of $\delta^{18}\text{O}$ values ever reported from marine sediments¹⁹, ranging from +12‰ to –25‰ (PDB) at centimetre-scale resolution (Fig. 2; Supplementary Table 1). Potential controls on oxygen isotope values include precipitating fluid temperature, fractionation associated with crystal formation, and the composition of the source pore fluid. The heaviest $\delta^{18}\text{O}$ values (Fig. 2; +12‰) occur in pore-filling dolomite cement and are too enriched in ^{18}O to be attributed to conventional mechanisms such as direct dolomite precipitation from sea water at 0°C (ref. 17). Values over 10‰ in marine sediments are known only from methane cold-seep environments where ^{18}O is enriched in pore fluids during methane clathrate formation and dolomite precipitation results from sulphate oxidation of methane^{17,20}. Values of $\delta^{13}\text{C}$ that range from –10‰ to +10‰ PDB (Fig. 2; Supplementary Table 1) within Reynella cements are also common within cold-seep-associated cements and attributed to

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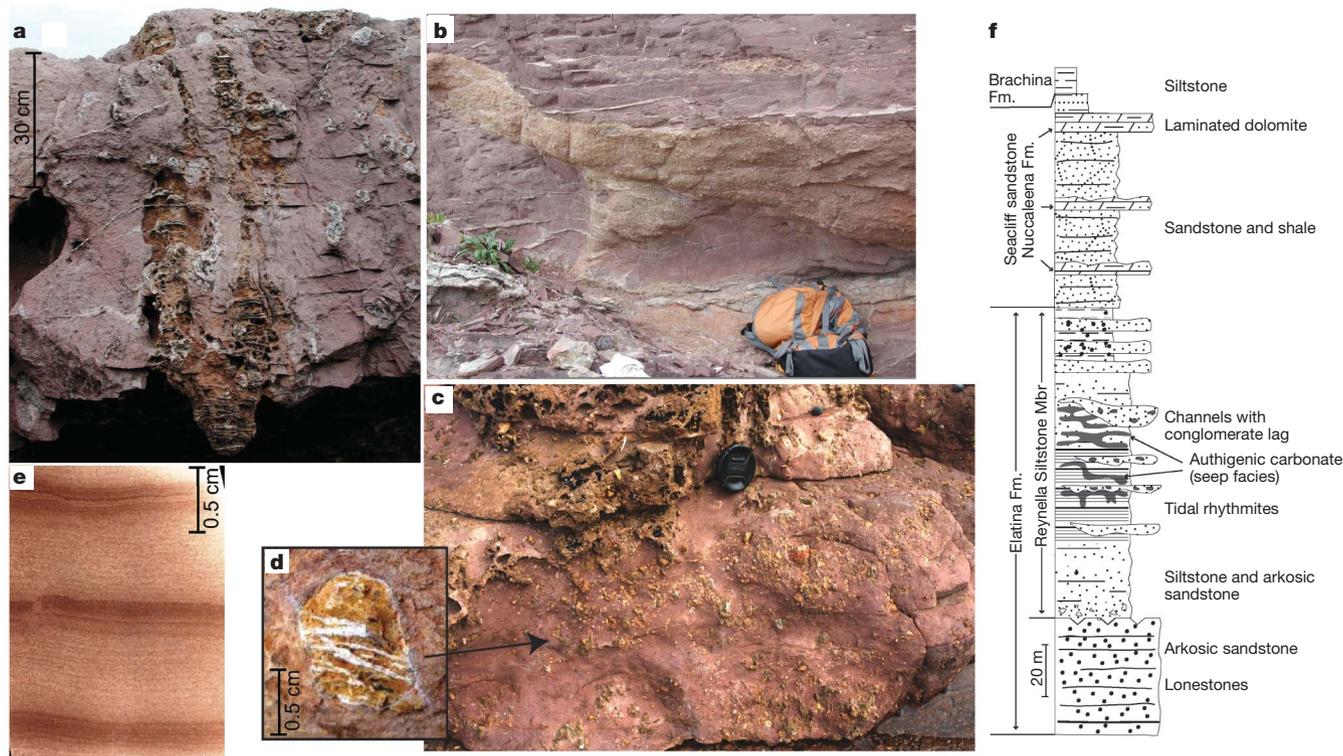


Figure 1 | Photographic examples and stratigraphic context for Reynella seep carbonates. Distinctive sedimentary facies include vertical cemented chimneys rising through coarse sandstone with sparry cavity cements (a); shallow channels (backpack for scale) with basal lags of authigenic carbonate clasts eroded from exhumed seeps (b); and breccia beds comprising cemented sandstone (5-cm lens cap for scale) resulting from

fluidization (c, d). A thin section of tidal rhythmites (e) shows well-developed neap–spring bundles of couplets from samples collected between authigenic carbonate hard grounds. Schematic section (f) shows the association of tidal, seep and stratigraphic units. Section and photos located between Hallet Cove and Marino Rocks around 36° 03' 45" S, 138° 30' 05" E.

concurrent methanotrophy and mixing between isotopically heavy methanogenic CO₂ and marine bicarbonate^{17,18,20}.

Values of $\delta^{18}\text{O}$ for calcite cements within the Reynella Member define a mixing line with a highly depleted meteoric endmember (-25‰ PDB; $R^2 = 0.84$). Although low $\delta^{18}\text{O}$ values can occur during

metamorphism by equilibration at $>180\text{ °C}$, a metamorphic origin is incompatible with the presence of temperature-sensitive detrital, dioctahedral-smectite in the laminated mud fraction of the host rock which would have converted to illite above 100 °C (Supplementary Fig. 1; Supplementary Table 2). Thermal equilibration is inconsistent with (1) the microcrystalline morphology of the cement, (2) the isotopic heterogeneity on millimetre scales, and (3) the relatively heavy $\delta^{18}\text{O}$ values of the Nuccaleena cap carbonate and late-stage (tectonic) cross-cutting spar fill fractures (Fig. 2). The isotopic signature of the most depleted cements (-25‰) requires porewater values as low as about -28 to -30‰ (see Supplementary Information), which, in the modern hydrological cycle, is unique to meltwater released from glacial ice²¹. In the geological record, these low values are found only in thermally altered carbonate spar¹⁹ or formed from glacial meltwater in ancient carbonates^{22,23}.

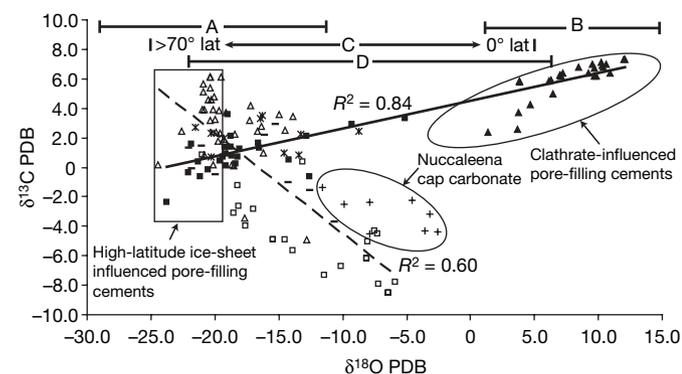


Figure 2 | Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for Nuccaleena Formation and Reynella Member cements and veins. Open triangles, calcite-cemented siltstone; filled triangles, dolomite-cemented siltstones; open squares, spar-filled cavities; filled squares, early calcite spar; asterisks, early spar-filled tubes; dashes, late cross-cutting veins; crosses, Nuccaleena cap carbonate. Upper trend comprises filled symbols and asterisks, lower trendline includes open symbols. Later phases (crosses and dashes) not included in trend lines. Horizontal bars represent ranges of $\delta^{18}\text{O}$ values from (A) isotopically light meltwater-related carbonates^{23,24}; (B) clathrate enrichment of ^{18}O in seep carbonates^{18,19,21}; (C) predicted $\delta^{18}\text{O}$ values from carbonate precipitated in 0 °C meteoric water from $>70\text{ ° latitude}$ (-26‰ PDB calcite from -30‰ SMOW water) to low latitude ($+4\text{‰}$ PDB from -2‰ SMOW water)²²; and (D) reported range of $\delta^{18}\text{O}$ values for all marine carbonate rocks³⁰.

The mixing relation connecting enriched and depleted $\delta^{18}\text{O}$ endmembers (Fig. 2), sub-centimetre spatial association and synsedimentary timing relations between stable isotopic endmembers indicates formation of seeps in a shallow environment in which meteoric fluid derived from an ice sheet mixed with ^{18}O -enriched clathrate-derived fluids. Such an environment occurs in shelf settings where the hydraulic drive of a melting ice sheet charges the water table, flushing and destabilizing clathrate fields.

Sedimentary evidence indicates that the Reynella seeps formed syndepositionally in high-energy, intertidal, sandstones. The authigenic carbonate occurs within a succession containing superbly preserved tidal bundles (Fig. 1e) including well-developed spring and neap cycles²⁴, broad (2 m), shallow (1 m) channels (Fig. 1b), reactivation surfaces, bimodal palaeocurrents within cross-bedded sands, and herringbone and flaser lamination, all indicative of a high-energy, macrotidal environment^{16,24} unique to coastal or estuarine settings. Reworking of authigenic carbonate in channels followed by

subsequent cementation (Fig. 1b) indicates that seep hard grounds formed throughout the tidally influenced deposition of sand.

Methane clathrates form when methane produced by thermogenic or biogenic breakdown of organic matter at depth migrates upwards to stabilize more than 200 m below the sea floor or land surface in a narrow range of pressure and temperature^{12,25}. To be stable, marine clathrates require both sea water at 0 °C and the additional pressure derived from more than 250 m of water¹². Because the Reynella Member consists of intertidal deposits within a deepening succession midway between the preceding glacial sealevel lowstand and the shelfal deposits of the Seaciff sandstone/Nuccaleena dolomite, the water could not have been deep enough to stabilize clathrates. The stabilization thus must have resulted either from the pressure of a shelf-borne ice sheet or from the permafrost conditions (<0 °C) indicated by local evidence of frost wedging²⁶. Permafrost clathrates that accumulated beneath the broad exposed shelves of the Arctic during the Pleistocene are now destabilizing as a result of post-glacial flooding and global warming^{11,12,25}. Similarly, retreat of the Marinoan ice sheet would have destabilized methane clathrates by (1) reducing hydrostatic pressure, (2) warming permafrost shelves with flooding sea water, and (3) flushing clathrate fields with meteoric water derived from meltwater discharge^{9,22,23}.

The extension of a volatile permafrost clathrate pool to equatorial palaeolatitudes has important implications for the role of methane in the climate system. Initial warming or, more simply, inherent ice-sheet instability²⁷, might have been enough to trigger local methane destabilization through meteoric flushing of the permafrost clathrate field on the Marinoan shelf, particularly in this low-latitude setting² where it was most sensitive to subtle external forcing. Once initiated, clathrate destabilization provides a positive feedback through greenhouse warming caused by methane and CO₂, and is amplified by further destabilization in progressively higher latitudes^{9,11} of permafrost and eventually marine clathrates. Extension of the Holocene permafrost reservoir, occurring over the Arctic shelves and estimated²⁵ at 400 gigatonnes, to total present-day shelf area (including low latitudes) could increase the potential size to ~3,000 Gt (see Supplementary Information). This estimate is conservative because it does not include the extensive intracratonic basinal areas characteristic of the Neoproterozoic (for example⁹), nor does it consider destabilization of the more conventional and tenfold larger marine clathrate reservoir²⁵. It is, however, comparable to past gas hydrate events with estimated releases of ~5,000 Gt in the Toarcian¹⁴ or ~1,000–2,100 Gt in the Palaeocene¹⁵ estimated from marine excursions of –7‰ and –3‰ δ¹³C, respectively. Permafrost clathrate destabilization could readily provide a trigger for feedbacks to deglaciation such as albedo, marine clathrate destabilization or carbonate reallocation^{3,28}.

Alkalinity increase capable of accounting for cap carbonate deposition could arise on shorter timescales (<10⁴ yr) from sulphate oxidation of methane following exhaustion of dissolved oxygen in pore and sea water¹⁰ and on longer timescales (>10⁵ yr) from oxidation of methane to CO₂ in the atmosphere driving increased continental chemical weathering. The duration of methane release would most likely be controlled by pulsed marine clathrate destabilization similar to that in the early Toarcian¹⁴, which occurred over ~200 kyr. Like other later methane destabilization events¹⁴, release of 3,000 Gt of methane (~2 × 10¹⁷ moles of carbon, excluding marine clathrates) into sea water over about 10³–10⁴ yr could substantially influence the redox state of parts of the ocean, significantly depleting the dissolved oxygen pool and consuming marine sulphate which maintained a probable stock of less than 4.5 × 10¹⁶ mole O₂ (ref. 29) and 5 × 10¹⁷ mole SO₄ (refs 2–5) (see Supplementary Information). Significant sulphate oxidation of methane within pore and sea water predicts the observed 15‰ positive shift in marine sulphate δ³⁴S values⁵. The release of 3,000 Gt of –60‰ δ¹³C methane from the permafrost reservoir could alone account for a shift of more than –3‰ (see Supplementary Information) of the enigmatic negative

δ¹³C excursion in marine carbonates that defines the base of the Ediacaran period⁴.

The distinctive features of Marinoan deglaciation that define the base of the Ediacaran period⁴ can be attributed to the effects of permafrost methane clathrate destabilization. In contrast to the balanced feedbacks and progressive glacial–interglacial cycles of Cenozoic deglaciation, the violent opening of the highly volatile shelf-permafrost methane clathrate pool could act as a trigger to catastrophic climate and biogeochemical reorganization of the Earth system, abruptly bringing the long-lived and icy Cryogenian period to a close and setting the stage for the appearance of metazoans and dominance of a new Earth system. This event both identifies the range of function of the climate system, and demonstrates a mechanism activated by strong climate forcing not unlike projected future effects of atmospheric CO₂.

METHODS SUMMARY

Detailed methods are given in the Supplementary Information. We characterized the petrography and mineralogy by X-ray diffraction, petrographic microscopy and back scattered electron microscopy. Isotopic results were obtained on a VG Isogas Prism II, with reproducibility of δ¹⁸O-enriched samples confirmed on a Thermo Delta-V Plus and at the University of California, Davis, and agree within 0.1‰. δ¹⁸O = [(¹⁸O/¹⁶O)_{sample} / (¹⁸O/¹⁶O)_{PDB}] – 1; δ¹³C = [(¹³C/¹²C)_{sample} / (¹³C/¹²C)_{PDB}] – 1.

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