Snowball Earth ocean chemistry driven by extensive ridge
volcanism during Rodinia breakup

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Abstract

During Neoproterozoic Snowball Earth glaciations, the oceans gained massive amounts of alkalinity, culminating in the deposition of massive cap carbonates upon deglaciation. Changes in terrestrial runoff associated with both breakup of the Rodinia supercontinent and deglaciation can explain some, but not all of the requisite changes in ocean chemistry. Submarine volcanism along shallow ridges formed during supercontinent breakup results in the formation of large volumes of glassy hyaloclastite, which readily alters to palagonite. Here we estimate fluxes of calcium, magnesium, phosphorus, silica and bicarbonate associated with these shallow ridge processes, and argue that extensive submarine volcanism during the breakup of Rodinia made an important contribution to changes in ocean chemistry during Snowball Earth glaciations. We use Monte Carlo simulations to show widespread hyaloclastite alteration under near-global sea ice cover could lead to Ca\textsuperscript{2+} and Mg\textsuperscript{2+} supersaturation over the course of the glaciation that is sufficient to explain the volume of cap carbonates deposited. Furthermore, our conservative estimates of phosphorus release are sufficient to explain the observed P:Fe ratios in sedimentary iron formations from this time. This large phosphorus release may have fuelled primary productivity, which in turn would have contributed to atmospheric O\textsubscript{2} rises that followed Snowball Earth episodes.

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Breakup of the Rodinia supercontinent contributed to profound environmental change during the Neoproterozoic (∼1000–540 Ma). It is thought that ice-sheets reached the equator\textsuperscript{1,2} and global temperatures dropped to −50°C during two long-lived ‘snowball’ events: the Sturtian (Cryogenian) glaciation at c. 720–660 Ma and the Marinoan (Varanger) glaciation at c. 650–630 Ma. These globally distributed glaciations have been attributed to major continental reconfiguration episodes\textsuperscript{3,4}. Protracted rifting around c. 750–725 Ma\textsuperscript{5} (lasting 100–120 Myr) formed the Proto-Pacific Ocean (Fig. 1a). The Sturtian glaciation coincided with initial breakup in Canada at c. 720 Ma\textsuperscript{6}, and the Marinoan with a later phase of the same breakup event in Antarctica from 670–650 Ma\textsuperscript{7}. Another major breakup event between c. 615 Ma\textsuperscript{8} and 550 Ma\textsuperscript{9} formed the Iapetus Ocean (Fig. 1b), concurrent with the Gaskiers glaciation at c. 582–580 Ma.

It has been suggested that (a) continental breakup led to sharp increases in riverine runoff and silicate weathering (including flood basalts\textsuperscript{10}), causing enhanced CO\textsubscript{2} drawdown and descent into a ‘snowball’ state; and (b) deglaciation resulted from gradual accumulation of atmospheric CO\textsubscript{2}\textsuperscript{11}, likely from subaerial volcanic outgassing\textsuperscript{12}, to critical levels capable of overcoming an ice albedo effect\textsuperscript{2}. Intense debate centres on the source of alkalinity required to form the extensive cap carbonate sequences associated with Snowball Earth termination, and their negative $\delta^{13}$C signatures\textsuperscript{2,12,13}. Carbonate sedimentation may have occurred rapidly (<10 kyr)\textsuperscript{12} due to a post-glacial greenhouse weathering spike\textsuperscript{14,15} of similar duration to Quaternary deglaciation\textsuperscript{16}. However, magnetopolarity reversals exhibited in some Marinoan cap carbonates suggest accumulation took place over longer timescales (≥100 kyr)\textsuperscript{17,18}. Similarly, meltback alone cannot easily explain the inferred increase in dissolved oceanic phosphate concentrations during the Tonian and Cryogenian periods\textsuperscript{19}. Despite the temporal coincidence between breakup of Rodinia and glaciations\textsuperscript{3,4}, as yet no studies have investigated the direct impacts of volcanism associated with extensive spreading ridge formation (Supplementary Information (SI) Fig. 1).

**The shallow ridge hypothesis**

Here we propose the novel shallow ridge hypothesis, which invokes ridge volcanism to drive efficient and long-lived seafloor alteration, and in conjunction with other weathering processes linked to continental breakup\textsuperscript{4,10,20} can reconcile many key features of Snowball Earth episodes.

Continental unzipping of the type associated with the breakup of Rodinia is accompanied by enhanced rifting and magmatism, and can coincide with an order of magnitude increase in magmatic productivity\textsuperscript{21}. The early phase
of ocean crustal development involves a period of relatively shallow marine
volcanism (Fig. 1c), as the ridge axis gradually subsides. This low hydro-
static pressure regime favours explosive fragmentation of lava in contact with
seawater, yielding voluminous hyaloclastite—a pyroclastic rock dominated
by juvenile angular glass fragments—along the newly formed ridge (Fig. 1d).
Hyaloclastite volcanism in early rifting environments is a rapid, high-volume
process, forming from volcanic centres 30–40 km wide, and producing mounds
∼1.5 km high and 15–20 km wide. Observations and empirical subsidence
relationships indicate that conditions favourable for hyaloclastite formation
(depths up to 2 km) would persist along the ridge for at least 20 Myr (SI Fig.
2).

The quenched glass shards typical of basaltic hyaloclastites are very suscep-
tible to alteration, largely by hydration to palagonite. This is enhanced by
a high reactive surface area:volume ratio and high porosity (compared to pil-
low lavas) that greatly increases seawater interaction. Basaltic glass alteration
involves considerable element mobilisation (e.g. Ca losses of ∼90%), thus
has the potential to exert a major control on seawater chemistry, including
consumption of aqueous CO2. The shallow ridge is also a major source of
magnesium, with basaltic glass experiencing Mg losses of ∼67% to ∼97%. Dissolution rates of basaltic glass could be reduced at the low temperatures
expected in an ice-covered ocean, but our model purely evaluates the initial
element flux during rapid quenching, followed by cation leaching, and does
not require total glass dissolution. As hyaloclastites accumulate in thick ‘piles’
along the ridge axis, they are susceptible to high temperature hydrothermal
circulation leading to further losses through diffusion—conditions thought
to persist for ∼106 yr. Conservatively, we only consider contributions from
freshly erupted material close to the ridge axis. Palagonitization of basaltic
glass occurs rapidly at high temperatures, and potentially within one year
in hydrothermal systems. Thus, hyaloclastite alteration can be considered
almost instantaneous on geological timescales.

This global scale process offers an alternative, complementary explanation for
the surge of alkalinity associated with the Neoproterozoic “calcium ocean” and
carbonate sedimentation, which cannot be satisfactorily explained by terres-
trial weathering alone. The process can also help explain the late Neopro-
terozoic ‘excess phosphate ocean’ and high concentrations of SiO2 in banded
iron formations (BIF). Although we focus on Rodinia, shallow ridge effects
will have similarly large impacts on ocean fluxes during any major episode
of continental breakup, albeit manifest in different ways due to variations in
timescales and extent of magmatic productivity, alteration and biological pro-
ductivity in the ocean. It is unclear why Pangea break-up did not result in
global glaciation, although the more polar location of continents may have
suppressed the continental silicate weathering CO2 sink.
The 750–725 Ma breakup involved at least $\sim 2 \times 10^4$ km spreading-ridge formation around the perimeter of Laurentia (Fig. 1a). Subsequent rift and drift episodes\(^3,5\) may have increased the total length of new spreading ridges by 3–4 times. Although Neoproterozoic ocean crust is poorly represented in the geological record (e.g. due to subduction), there is evidence for widespread hyaloclastite emplacement during breakup, prior to ‘snowball’ glaciations (Fig. 2). For example, the 717–716.5 Ma Mount Harper Volcanic Complex\(^6\)—a 1.6 km thick succession of subaqueous hyaloclastites, breccias and lavas emplaced along the rifted northwestern Laurentian margin\(^31\)—is directly overlain by Sturtian glacial diamictites. Rift-related volcanism would have continued during glaciations (SI Table 1), as newly formed ocean crust progressively unzipped to form the extensive Proto-Pacific ridge system. Crucially, and in contrast to most other biogeochemical fluxes, hyaloclastite-derived ocean fluxes will not have been affected by near-global ice cover.

There is also evidence for extensive volcanism, again associated with Rodinia breakup, prior to the Marinoan glaciation (e.g. 670–650 Ma in Antarctica\(^7\); Fig. 2). The apparent ‘delay’ in initiation of rifting between Laurentia and Antarctica confirms that breakup was protracted\(^3\), and seafloor spreading continued throughout the Sturtian and Marinoan glaciations. Similarly, basaltic hyaloclastites associated with the early opening of Iapetus ($\sim 615–580$ Ma) are recognised globally (Fig. 2; SI Table 1). Hyaloclastites are directly overlain by diamictites associated with the Gaskiers glaciation\(^32\), signifying explosive shallow marine volcanism before (and likely during) the Gaskiers event (Fig. 2).

Better time constraints in the Neoproterozoic are needed to explore whether shallow ridge volcanism could have played a key role in initiating snowball glaciation. However, this is feasible given: (1) an intrinsic need for continental breakup in order to intensify silicate weathering\(^4,10\), and (2) isotopic evidence for copious weathering of juvenile mantle-derived volcanics before the Sturtian glaciation\(^33\).

### Hyaloclastite alteration fluxes into the ocean

We develop Monte Carlo simulations to quantify potential chemical fluxes (Ca, P, Si, Mg) into the ocean during shallow ridge volcanism. Given the significant uncertainties in initial conditions and fluxes (e.g. seawater chemistry, pH), this situation does not lend itself to deterministic modelling, but instead must be probabilistically assessed. Here, we present a parsimonious model, supported
by observations and experiments (Table 1, methods), broadly capturing the key processes and associated uncertainties. Ridge length is varied from 0.5 to 2 × 10^4 km to simulate progressive separation of Laurentia, and full spreading rates from 50 to 200 mm yr\(^{-1}\) to represent moderate to fast rates expected during breakup. The simulations account for secondary mineral formation, for example carbonate fluorapatite (CFA) formation following release of P\(_2\)O\(_5\) during glass alteration, and smectite (saponite) formation as a sink for silica. Fluxes calculated here exclude background seafloor weathering and hydrothermal processes associated with contemporary deep ridge systems, e.g. in the Mirovia superocean (Fig. 1a), which would increase Ca, P, Si and Mg oceanic input.

Hyaloclastite formation rates (and hence magnitude of the chemical fluxes) vary spatially and temporally during ridge formation, hence our deliberately wide and conservative parameter ranges (Table 1). All input distributions are sampled independently because of insufficient observational evidence to accurately define correlations, but three more tightly constrained scenarios (SI Table 2) explore sensitivity of the calculated fluxes to independence assumptions. The high hyaloclastite production scenario (I, SI Table 2) involves both rapid and spatially extensive unzipping. A further simulation explores the potential correlation between ridge length and magmatic productivity, arising from the temporal evolution of the ridge system.

Given CaO losses from hyaloclastites range from 4–10 wt%\(^{24,25}\), our simulations suggest optimal spreading conditions along the length of the Proto-Pacific ridge could yield a maximum Ca flux of 1.4 × 10\(^{13}\) mol yr\(^{-1}\) (Fig. 3a; SI Fig. 3a); comparable to the modern dissolved riverine flux of \(\sim\)1.2 × 10\(^{13}\) mol yr\(^{-1}\) (ref.\(^{37}\)) and 1–3 orders of magnitude greater than the modern hydrothermal ridge flux (9–1300 × 10\(^9\) mol yr\(^{-1}\))\(^{38}\). Glass alteration also results in uptake of CO\(_2\) from solution\(^{39}\) according to the approximate reaction:

\[
\text{Reactive silicates} + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{dissolved cations} + \text{clay minerals} \quad (1)
\]

Ca forms most of the charge balance carried by the dissolved cation budget released to solution during glass alteration. Mg and Na contribute most of the remainder, along with a small uptake of K\(^{24}\). Thus, a combined Ca, Mg and Na (–K) flux of approximately 2 × 10\(^{13}\) mol yr\(^{-1}\) during hyaloclastite alteration results in uptake of 4 × 10\(^{13}\) mol yr\(^{-1}\) of CO\(_2\). By comparison, the global rate of continental silicate weathering is 1.2 × 10\(^{13}\) mol yr\(^{-1}\) of CO\(_2\) (ref.\(^{40}\)).

Hyaloclastite alteration in an ice-covered ocean provides a major source of alkalinity—additional to that provided by the long-term alteration of the oceanic crust\(^{20}\)—driving up carbonate production immediately after Snowball Earth glaciations. The cap carbonate sequences that formed globally on con-
tinental margins, typically overlying glacial diamictites\textsuperscript{2,12}, are commonly attributed to enhanced terrestrial weathering of carbonate-rich sediments during and after glaciation\textsuperscript{14,15}. However, to achieve observed cap carbonate thicknesses (some >100 m, Figs 3c,d) would require extreme levels of terrestrial weathering, delivering $\sim 10^2$–$10^3$ times the present annual supply of dissolved cations to the oceans\textsuperscript{29}. Continental runoff during the post-snowball greenhouse ($400 \times$ modern $p\text{CO}_2 \text{ atm}$) likely produced $\sim$1.2 times the modern riverine runoff\textsuperscript{16}, suggesting subaerial weathering alone cannot explain cap carbonate production\textsuperscript{29}.

We propose that under near-global ice cover, which suppresses normal removal processes, a prolonged state of hyaloclastite eruption and alteration would supersaturate seawater with Ca\textsuperscript{2+} and Mg\textsuperscript{2+}. This is consistent with evidence for rapid carbonate sedimentation (spontaneous nucleation) following glaciations\textsuperscript{2,12,15}. The question is whether requisite degrees of supersaturation are feasible over such prolonged timescales (order 10 Myr). At our maximum estimated discharge rate (the trivial case with no initial dissolved Ca\textsuperscript{2+} or Mg\textsuperscript{2+}) the ocean reaches saturation within 1–3 Myr (Ca\textsuperscript{2+} and Mg\textsuperscript{2+}, respectively).

A 10 Myr glaciation could therefore yield degrees of supersaturation exceeding 12$\times$ (Ca\textsuperscript{2+}) and 3$\times$ (Mg\textsuperscript{2+}), certainly feasible in the light of observations of experimental solutions\textsuperscript{41}, geological fluids\textsuperscript{42}, and the present-day surface ocean\textsuperscript{43}. In the glacial aftermath, conditions become more favourable for rapid precipitation: higher ocean temperatures, renewed photosynthesis, increased primary productivity, enhanced atmospheric CO\textsubscript{2} exchange, and importantly, resumption of particle settling providing carbonate condensation nuclei. Volcanism before and after glaciations (Fig. 2; SI Table 1) will also have contributed to carbonate deposition, although in the absence of ice cover (limiting build-up in the ocean) would occur more gradually. Combined with the rate-limiting influence of platform subsidence\textsuperscript{2}, this may explain slower sedimentation rates inferred for some Marinoan carbonate sequences\textsuperscript{17,18}.

In an ice-covered ocean, limited atmospheric exchange leads to rapid conversion of dissolved CO\textsubscript{2} to bicarbonate (HCO\textsubscript{3}–, which constitutes the majority of seawater DIC) by equation [1]. However, hyaloclastite formation is also associated with CO\textsubscript{2} degassing from erupted basalt, particularly at shallow depths. Assuming a pre-eruptive CO\textsubscript{2} concentration of 0.5 wt% in the basalts and total degassing, hyaloclastite emplacement could release $\sim$0.03–1.3 $\times$ 10\textsuperscript{12} mol yr\textsuperscript{-1} CO\textsubscript{2}, broadly consistent with the ridge flux ($\sim$0.8 $\times$ 10\textsuperscript{12} mol yr\textsuperscript{-1}) assumed for the ‘snowball’ ocean\textsuperscript{2}. This is not a completely closed system: cracks in sea-ice\textsuperscript{44} will have permitted some CO\textsubscript{2} outgassing. Equally, ice-free regions will have allowed CO\textsubscript{2} ingassing during a period when atmospheric CO\textsubscript{2} levels due to subaerial volcanism\textsuperscript{2} ultimately exceeded present-day levels by two to three orders of magnitude\textsuperscript{11}, a net CO\textsubscript{2} gain. The long-term CO\textsubscript{2} input from volcanism and hydrothermal activity can explain mantle-like $\delta^{13}$C signatures ($\sim$6 ± 1‰) observed in many cap carbonates\textsuperscript{2,12,13}. Stratigraphic or localised carbon-
ate $\delta^{13}$C increases may reflect increases in biological productivity, organic carbon burial, and intensified subaerial carbonate weathering—all expected in the snowball aftermath.

Some post-Sturtian cap carbonates exhibit $^{187}$Os/$^{188}$Os ratios consistent with continental inputs, again expected during a post-glacial weathering spike. However, many cap carbonates exhibit only minor shifts in $^{87}$Sr/$^{86}$Sr (refs. 15,29), suggesting that enhanced terrestrial weathering was not dominant in their production. Pre-Marinoan carbonates (800–650 Ma) exhibit relatively low $^{87}$Sr/$^{86}$Sr (ref. 45), compatible with significant hydrothermal ridge contributions, which will progressively dominate the Sr isotope inventory in seawater under ice cover with much reduced continental runoff. Further, widespread enrichment of heavy rare earth elements (REE) and positive Eu and Y anomalies in Sturtian and Marinoan cap carbonates can be explained by alteration of mid-ocean ridge basalts and wholesale mixing of hydrothermal fluids in the ocean.

The maximum simulated Ca$^{2+}$ flux (Fig. 3a) would yield $\sim$18.5 m-thick build-up (mean estimate 2 m, median 1.2 m, Fig. 3c) of carbonate over an area equivalent to the present-day continental shelf for every 10$^6$ years of ridge formation. Given the Sturtian (diachronous) and Marinoan glaciations persisted for $\sim$55 Myr and $\sim$12 Myr, respectively, these accumulations are of the same order as observed cap carbonates, typically metres to tens of metres thick (Fig. 3c).

Ridge alteration could produce magnesium fluxes of the order $1$–$6 \times 10^{12}$ mol yr$^{-1}$ (Fig. 3b and SI Table 2; modern riverine Mg flux is $5.1 \times 10^{12}$ mol yr$^{-1}$), potentially contributing $\sim$2–15 m-thick dolostone for every 10$^6$ years of ridge formation. Accordingly, our model suggests the Marinoan event could yield 20–150 m-thick dolostone, consistent with observed global mean and maximum thicknesses of 18.5 m and 175 m respectively (Fig. 3d). On timescales typically associated with deglaciation (c. 10 kyr), continental weathering is only likely to supply enough Mg$^{2+}$ to produce a $\sim$0.5 m thick cap dolostone. Therefore our hypothesis provides an important or even dominant additional source of Ca$^{2+}$ and Mg$^{2+}$, and can help explain not only the qualitative association of cap carbonate and dolostone sequences with Snowball Earth episodes, but also observed thicknesses of these deposits.

Although up to 90% P$_2$O$_5$ in fresh basaltic glass can be released during alteration, we assume a conservative 20–80% loss, based on modern palagonites. Simulations show that high spreading rates (>100 mm yr$^{-1}$) coupled with extensive ridges (>15 $\times$ 10$^3$ km), could yield dissolved phosphorus fluxes up to $7 \times 10^{11}$ mol yr$^{-1}$ (Fig. 4a; SI Fig. 3b), roughly 20 times the modern dissolved riverine flux ($3.1 \times 10^{10}$ mol yr$^{-1}$). For the full simulation (SI Table 2), the median phosphorus flux ($3.7 \times 10^{10}$ mol yr$^{-1}$) is comparable to the modern
riverine contribution, and the high hyaloclastite production scenario yields a flux \(\sim 7\) times greater \((2.3 \times 10^{11} \text{ mol yr}^{-1}; \text{Fig. 4b})\). Assuming full unzipping and substantial secondary mineralisation losses (SI Fig. 4), there is \(\sim 70\%\) probability that P-influx would exceed the modern riverine flux (SI Fig. 5). In the modern ocean, phosphate sorption onto ferric oxyhydroxides represents a significant sink, but this is thought to have been of minor importance in the Neoproterozoic due to high oceanic silicic acid concentrations—as silica hydroxides suppress phosphate sorption onto ferric oxyhydroxides\(^{19}\).

Hyaloclastite alteration during ridge unzipping provides a viable mechanism to account for anomalously high seawater phosphorus levels (5–10 times Phanerozoic levels, according to P:Fe ratios in sedimentary iron formations)\(^{19}\) inferred for Snowball Earth episodes. This ‘excess phosphate ocean’ has been attributed to enhanced weathering of glacial deposits during the ‘snowball’ thaw phase\(^{19}\). Although relevant, post-glacial weathering would be expected to yield a relatively short-lived (\(\sim 10–100\) kyr\(^{16}\)) increase in phosphate, and could be problematic in view of the low solubility of apatite. Our model provides a mechanism for producing high dissolved phosphorus levels that, in the absence of biological removal, could persist over \(\sim 10–100\) Myr (Fig. 2), over repeated cycles (i.e., protracted opening of the Proto-Pacific followed by Iapetus in Ediacaran times; Fig. 1b\(^3\)). This process operated independently, and in addition to other mechanisms, such as biotic enhancement of apatite weathering linked to increased weathering rates via microbial colonisation of the land\(^{53}\), and subaerial weathering of large igneous provinces\(^{54}\) (notably during the Tonian period; Fig. 2).

The shallow ridge can also contribute to relatively high dissolved oceanic silicic acid concentrations inferred for the Neoproterozoic\(^{19}\), and the SiO\(_2\)-rich (\(\sim 30–55\%\)) banded iron formations (BIF) that served as a (local) silica sink during the Sturtian\(^{30,55}\), and possibly, but not ostensibly, during the Marinoan\(^{55}\) glaciations. Basaltic glass alteration results in loss of an average \(\sim 16\) wt\% SiO\(_2\)\(^{24}\) (potentially up to 50\%)\(^{25}\), thus contributing up to \(10\times\) the current riverine flux of \(\sim 6.4 \times 10^{12} \text{ mol yr}^{-1}\) (ref.\(^{37}\)) to the ocean during extensive hyaloclastite alteration (SI Table 2, SI Fig. 6b). High hydrothermal Fe fluxes\(^{48}\) are expected in our low hydrostatic pressure regime\(^{56}\), and a dominance of hydrothermal inputs is supported by mantle-like Nd and Pb isotope signatures observed in some BIFs\(^{30}\). Thus, our hypothesis might help elucidate the common association between BIFs and mafic volcanics\(^{55}\), although this requires further validation, particularly given the localised nature of many BIFs.
Consequences of a shallow ridge system

The discovery that Earth experienced near-total ice cover for prolonged periods in the Neoproterozoic has greatly enhanced understanding of Earth history, but critical aspects remain unresolved. We demonstrate how enhanced shallow marine volcanic activity, persisting for >20 Myr in the absence of most biological removal processes, would have driven major changes in ocean chemistry. Our shallow ridge hypothesis advances understanding of Snowball Earth events, qualitatively and quantitatively explaining many enigmatic features including: increased ocean alkalinity; $^{13}$C-depleted cap carbonate sequences; and high silica concentrations manifest in banded iron formations.

Our hypothesis provides a critical quantitative explanation for unusually high dissolved phosphate inputs to late Proterozoic oceans. This enhanced supply likely drove the increase in primary productivity required to generate the large rise in atmospheric oxygen levels that occurred in the wake of Snowball Earth events\textsuperscript{19}. We infer that shallow ridge volcanism associated with the Proto-Pacific and Iapetan rifts also prompted oxidation of the Ediacaran ocean\textsuperscript{57}, which would have facilitated the emergence of multicellular life.

Methods

Methods and any associated references are available in the online version of the paper.

References


19. Planavsky, N. J., Rouxel, O. J., Bekker, A., Lalonde, S. V., Konhauser,


33. Rooney, A. D., Macdonald, F. A., Strauss, J. V., Dudás, F. Ö., Hall-


48. Huang, J., Chu, X., Jiang, G., Feng, L., and Chang, H. Hydrothermal origin of elevated iron, manganese and redox-sensitive trace elements in
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Author contributions

The research was conceived and managed by T.G. T.H. developed and performed simulations with inputs from T.G., T.T., M.R.P. and E.J.R. The manuscript was written by T.G. with important contributions from all co-authors.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permission information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to T.G.

Competing financial interests

The authors declare no competing financial interests.
Figure 1 | Evolution of spreading ridge systems during the late Neoproterozoic. a. Continental reconstructions at ∼750 Ma showing location of the Proto-Pacific rift system, and b, at ∼600 Ma showing inferred location of the Iapetan rift (modified after ref. 10). c. During the early phase of plume magmatism (∼800 Ma), volcanism was largely subaerial (Supplementary Information Table 1); however, as rifting occurred, the main axis of volcanism submerged below sea-level resulting in the formation of the Proto-Pacific (and Iapetus at ∼600 Ma) and a sustained phase of shallow marine volcanism. d. Under these conditions (shown here prior to glaciation), hyaloclastites are formed preferentially by quenching and explosive shattering of lava in contact with seawater, forming ‘fresh’ highly alterable glasses.

Figure 2 | Summary of major global volcanic events during the Tonian, Cryogenian and early Ediacaran periods, in relation to major glaciations (blue) and continental breakup events (beige). Red bars signify major volcanic events involving extensive hyaloclastite emplacement (see Supplementary Information Table 1 for more information); note LIP: Large Igneous Province; ANS: Arabian-Nubian Shield.

Figure 3 | Monte Carlo simulations showing estimated Ca and Mg fluxes into the ‘snowball’ ocean, and resulting thicknesses of carbonate and dolostone. Input parameter ranges are defined in Table 1. Note the logarithmic scales for the flux axes in (a) and (b). a. Flux of Ca, accounting for a variable percentage lost to CaCO₃ cementation. b. Flux of Mg, accounting for in situ dolomite cementation; lines denote the modern annual riverine dissolved Ca and Mg fluxes for comparison. Note that (a) and (b) represent the full simulation (SI Table 2). c. & d. Probability of exceedance for cap carbonate (c) and dolostone (d) thicknesses resulting from accumulation of Ca and Mg, respectively, in seawater over the course of a Snowball Earth episode of 10 Myr duration. The shaded areas show typical (grey) and maximum (light grey) observed thicknesses: 3–30 m for CaCO₃ (maximum 400 m)¹²; and 1.5–38 m for CaMg(CO₃)₂ (maximum >175 m)⁵². The curves show the probability, based on all simulations, that a given thickness will be exceeded; e.g. for the full simulation (black line) shown in (c), more than 40% of simulations exceed the observed mean of carbonate thickness (∼18.5 m), and 20% exceed 30 m. Curves are shown for the full simulation (black line) and three alternative ridge productivity scenarios (I-III) defined in SI Table 2.

Figure 4 | Monte Carlo simulations for estimated phosphorus fluxes into a typical ‘snowball’ ocean. Input parameter ranges are defined in Table 1. Note the logarithmic scale for the flux axis in (a). a. Flux of P,
accounting for CFA cementation (Supplementary Information Fig. 4). Solid line denotes the modern annual dissolved riverine P flux for comparison. b. Probability of exceedance of phosphorus fluxes computed for the full simulation (black line) and three alternative ridge productivity scenarios (I–III) defined in SI Table 2 (see Supplementary Information Fig. 5 for the effects of CFA cementation).

Tables

Table 1 | Ranges of parameter values used in the Monte Carlo simulations. See Methods for further details.

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<tr>
<th>Sampled parameters</th>
<th>Minimum value</th>
<th>Maximum value</th>
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<td>$R$ = Ridge length (m) (ref. 3)</td>
<td>$0.5 \times 10^7$</td>
<td>$2 \times 10^7$</td>
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<td>$S$ = Spreading rate (m yr$^{-1}$) (refs 5,34,35)</td>
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<td>$D$ = Alteration (penetration) depth (m) (ref. 36)</td>
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<td>1500</td>
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<td>$H_s$ = Fraction hyaloclastite from 0–1 km depth (ref. 23, Methods)</td>
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<td>0.2</td>
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<td>$L_{SiO_2}$ = Fraction SiO$_2$ loss (ref. 24,25)</td>
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<tr>
<td>$C_{CaO}$, $C_{CFA}$, $C_{SiO_2}$, $C_{MgO}$ = Cement phase (as fraction of element loss)</td>
<td>0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Methods

Deposition of chemically easily weathered hyaloclastites will cause a major influx of Ca, P, Si and Mg, among other elements, into the oceans. Monte Carlo simulations were performed to capture the variation in the main depositional and weathering processes. Input parameters were sampled independently from uniform distributions over fixed intervals, given in Table 1 (using the Scythe C++ Statistical Library). Uniform distributions were chosen as these yield the most conservative estimate of uncertainty, and there is not enough observational evidence to justify a more tightly constrained distribution (e.g. specifying a central weighting would require knowledge of the mean and variance of the distribution). The model generates a volume of hyaloclastite (m$^3$ yr$^{-1}$), given a sampled total ridge length ($R$), spreading rate ($S$) and cumulative deposit thickness ($D$). The annual elemental flux estimates (Figs 3a,b) are based on annual ridge output (fresh material along the hot ridge...
axis). Any subsequent contributions from previously unaltered erupted products are conservatively excluded. Long-term accumulation in the ocean (over the period of active rifting) (Figs 3c,d) is estimated by summing the (variable) annual elemental contributions over a period of 10 Myr, again a conservative estimate of the time during which we would expect extensive hyaloclastite formation and alteration. We therefore account for short-term fluctuations in calculating cumulative oceanic inputs, and potential deposit (cap carbonate) thickness. The ridge length is varied from $5-20 \times 10^3$ km to simulate progressive breakup of Rodinia around the perimeter of Laurentia. The spreading rate is varied from 0.05–0.2 m yr$^{-1}$ to simulate moderate to fast rates expected during breakup. Here, the higher rate is not unreasonable, given that Laurentia is known to have moved at speeds of 0.2 m yr$^{-1}$ during the Ediacaran.

Conservatively we consider a range of alteration penetration depths from 100–1500 m. Through analogy with ophiolite sequences, hyaloclastite deposit thickness and other parameters will vary with depth. In the upper kilometre, the hyaloclastite (i.e. pyroclastic) fraction ($H_s$) ranges from 50–80% of the total bed depth, reflecting the observed tendency for enhanced explosivity in shallow water conditions (<1 km). Below 1 km hyaloclastites are expected to be less extensive (10–20% of bed depth) due to an overriding tendency for intrusive processes at depth in ocean crust. Again conservatively we assume no hyaloclastite below 1.5 km. These estimates are consistent with deposits observed along analogous rifted margins.

The equations used in simulations are given below (for definitions, see Table 1 and Supplementary Information Tables 3 & 4).

Equation [2] gives the total thickness of hyaloclastite deposits, and [3] the corresponding mass of hyaloclastite formed per year along the length of the ridge. Equation [4] gives the approximate mass of $P_2O_5$, CaO, SiO$_2$ or MgO lost due to hyaloclastite alteration. This can either be released to the ocean or consumed during cement formation.

$$\begin{align*}
\begin{cases}
t_s = DH_s & \text{if } D \leq 1000 \text{ (m)} \\
t_d = 0 & \\
\end{cases}
\end{align*}$$

$$\begin{align*}
\begin{cases}
t_s = 1000H_s & \text{if } D > 1000 \text{ (m)} \\
t_d = (D - 1000)H_d & \\
\end{cases}
\end{align*}$$

$$m_{\text{total}} = RSP_{\text{crust}}(t_s(1 - \Phi_s) + t_d(1 - \Phi_d))$$

$$m_{P_2O_5/ CaO/ SiO_2/ MgO} = m_{\text{total}} P_{L/P_2O_5/ CaO/ SiO_2/ MgO}$$

Hyaloclastite volume will also be affected by porosity, which below 1 km depth ($\Phi_d$) is taken to range from 0.08–0.12 (ref. 66), and above 1 km ($\Phi_s$), where there is less compaction, from 0.12–0.3 (refs 64,71). Given that the volcanic environment
and regime will largely generate fine-grained glass particles, and considering the relatively high porosities and reactive surface areas, we consider an altered fraction ($P$) ranging from 0.6–1.0, again typical of natural examples\textsuperscript{74}. The resulting deposit is then subject to elemental losses (i.e., flux into the ocean and cement formation). For example, Ca losses ($L_{CaO}$) are assumed to range from 0.04–0.1 of the altered fraction, as observed in natural samples\textsuperscript{72,73}. These input distributions represent the main processes affecting annual variability in elemental flux.

A component of the elemental losses will form pore-filling cements and the remainder is assumed to go directly into the ocean. Cement fraction ($C_{CaO}$) is highly variable in nature\textsuperscript{71}. We therefore allow it to range from 0–1.0 of the total amount of the leachate, and consider secondary phases that result in relatively high losses of elements. For calcium, we consider CaCO$_3$ containing $\sim$56\% CaO, while saponite clays (smectite) only contain $\sim$1.2\% CaO. This approach leads to a conservative estimate of ocean flux, particularly as cement formation typically takes place over longer timescales ($>10^5$ yrs)\textsuperscript{74,75}.

The model considers the formation of (i) carbonate fluorapatite (CFA) cement, with equation [5] giving the mass of P$_2$O$_5$ in cements, [6] the mass of CaO in cements, and [7] the total CFA cement mass; (ii) carbonate cement, with [8] giving the mass of CaO and [9] the total mass of CaCO$_3$ cement; (iii) saponite clays, with [10] giving the total mass of SiO$_2$ and [11] the total mass of saponite; and dolomite cement, with [12] giving the mass of MgO and [13] the total mass of CaMg(CO$_3$)$_2$ cement. In all cases the resulting mass released to the ocean is assumed to be $m^o = m - m^c$.

The numbers of moles of Ca, P, Si and Mg released to the ocean are given in [14], [15], [16] and [17]. Equation [18] gives the equivalent fraction of hyaloclastite pore space filled with cement or clay.

Carbonate fluorapatite (CFA) (kg yr$^{-1}$):

$$m_{P2O5}^c = C_{CFA}m_{P2O5} \quad (5)$$

$$m_{CaO}^c = \left(\frac{0.56}{0.36}\right)m_{P2O5}^c \quad (6)$$

$$m_{CFA}^c = \frac{100m_{P2O5}^c}{q_{P2O5}} \quad (7)$$

Carbonate cement (kg yr$^{-1}$):

$$m_{CaO}^c = C_{CaO}m_{CaO} \quad (8)$$
\[ m_{\text{CaCO}}^c = m_{\text{CaO}}^c + \left( w_{\text{CO}2} \frac{m_{\text{CaO}}^c}{w_{\text{CaO}}^{\text{mol}}} \right) \]  \hspace{1cm} (9)

Saponite-type clays (kg yr\(^{-1}\)):

\[ m_{\text{SiO}2}^c = C_{\text{SiO}2} m_{\text{SiO}2} \]  \hspace{1cm} (10)

\[ m_{\text{saponite}}^c = \frac{100 m_{\text{SiO}2}^c}{q_{\text{SiO}2}} \]  \hspace{1cm} (11)

Dolomite cements (kg yr\(^{-1}\)):

\[ m_{\text{MgO}}^c = C_{\text{MgO}} m_{\text{MgO}} \]  \hspace{1cm} (12)

\[ m_{\text{CaMg(CO)}3_2}^c = m_{\text{MgO}}^c + (2 w_{\text{CO}2}^{\text{mol}} + w_{\text{CaO}}^{\text{mol}}) \left( \frac{m_{\text{MgO}}^c}{w_{\text{MgO}}^{\text{mol}}} \right) \]  \hspace{1cm} (13)

Flux to the ocean (mol yr\(^{-1}\)):

\[ n_{\text{Ca}} = m_{\text{CaO}}^c \left( \frac{1000}{w_{\text{CaO}}^{\text{mol}}} \right) \]  \hspace{1cm} (14)

\[ n_{\text{P}} = 2 m_{\text{P2O5}}^o \left( \frac{1000}{w_{\text{P2O5}}^{\text{mol}}} \right) \]  \hspace{1cm} (15)

\[ n_{\text{Si}} = m_{\text{SiO}2}^o \left( \frac{1000}{w_{\text{SiO}2}^{\text{mol}}} \right) \]  \hspace{1cm} (16)

\[ n_{\text{Mg}} = m_{\text{MgO}}^o \left( \frac{1000}{w_{\text{MgO}}^{\text{mol}}} \right) \]  \hspace{1cm} (17)

Pore fill:

\[ f_{\text{fill}} = \left( \frac{m_{\text{c}}/\rho_{\text{cement}}}{(\Phi_s v_s) + (\Phi_d v_d)} \right) \]  \hspace{1cm} (18)

Input parameter distributions are deliberately and conservatively wide to simulate the full range of plausible conditions and high temporal and spatial variability during
ridge formation. Ocean flux estimates for three variant scenarios, corresponding to
(I) full unzipping with high hyaloclastite production, (II) full unzipping with moder-
ate hyaloclastite production and (III) partial unzipping with moderate hyaloclastite
production are presented to demonstrate model sensitivity to basic assumptions.
Supplementary Information Table 2 presents the full range of input distributions
for the full and variant scenarios.

Supplementary Information figure 3 shows the fluxes of (a) calcium and (b) phospho-
rus into the ocean as a function of spreading rate and accumulated deposit thickness
(using full simulation values in Supplementary Information Table 2). Supplemen-
tary Information figure 4 shows estimated hyaloclastite volumes, and the effect of
cementation on ocean flux of P. The specific effect of cementation on the phospho-
rus flux was also considered (Supplementary Information Fig. 5), and shows that
even cases involving high degrees of cement formation can still result in very high
dissolved phosphorus fluxes (relative to the modern riverine flux) for long ridges.
Supplementary Information figure 6 shows probability of exceedance for Ca and
Si for the variant scenarios (I, II and III in Supplementary Information Table 2),
alongside the full simulation.

A further simulation explores sensitivity to the temporal evolution of the rifting
process, accounting for likely (but difficult to constrain) correlations between ridge
length and magmatic productivity. Here we define three phases in the rifting pro-
cess, based on the parameters used for the full simulation (observed global, present
day averages): (A) Initiation, where ridge length is short (R = 5000–10000 km) but
productivity is high (S = 0.15–0.2 m yr\(^{-1}\), D = 1000–1500 m); (B) Mid-event (R
= 10000–15000 km, S = 0.10–0.15 m yr\(^{-1}\), D = 600–1000 m); and (C) Final stages
of rifting where the ridge has reached its full extent but productivity is very low
(R = 15000–20000 km, S = 0.05–0.10 m yr\(^{-1}\), D = 100–600 m). All other param-
eters are as defined in Supplementary Information Table 2 for the full simulation.
Supplementary Information figure 7 shows the probability of exceedance for annual
Ca flux for phases A, B and C, compared to the full simulation (shown in black).
This shows that although we cannot explicitly model correlations between param-
eters (e.g. arising from temporal evolution), the full and variant scenarios provide
a reasonable representation of cumulative fluxes over typical timescales associated
with unzipping of Rodinia (order 10 Myr). Unfortunately, there is insufficient ob-
servational evidence to apply covariance estimates to other parameters used in our
simulations. In the absence of robust evidence, any attempt to correlate parameters
(for example, cement fraction and depth) would decrease the uncertainty, thereby
reducing the spread of the output distributions and providing false certainty in the
outputs.

To reconcile the results of the simulation with observed post-snowball cap carbonate
and dolostone deposits, we estimate the thickness of precipitates that could form
after 10 Myr accumulation of oceanic Ca and Mg (Figs 3c-d). Taking the simulated
annual flux of Ca and Mg (mol yr\(^{-1}\)) as the average for the episode, and assuming
a final deposition area equivalent to the modern day continental shelf (A = 2.8 ×
10\(^{13}\) m\(^2\)) gives the following estimate for cumulative deposit thickness after 10 Myr:
\[ T = n^{mol} \times 10^7 \left( \frac{w^{mol}}{1000} \right) \left( \frac{1}{\rho A} \right) \]  

(19)

where \( n^{mol} \) is the number of moles \( yr^{-1} \) from our simulation, \( w^{mol} \) is the molar weight of either carbonate, \( CaCO_3 \) (100 g \( mol^{-1} \)) or dolomite, \( CaMg(CO_3)_2 \) (184.4 g \( mol^{-1} \)), and \( \rho \) is the density of the deposit, i.e. \( \rho_{CaCO_3} \) or \( \rho_{Dolo} \) (Supplementary Information Table 4).

**Code availability**

We have opted not to make the computer code associated with this paper available because it is currently being developed for another follow-up study, but will be released when this work is published.

**Methods references**


c. 750 Ma

- Continental flood basalt eruptions
- Upwarping

c. 800-750 Ma

- Plate divergence
- Plume relaxation

- Continental flood basalt eruptions

- Submarine explosive eruptive phase (see d)

- Subsiding shallow water basin

- Volcanic outgassing ($CO_2$), aerosols, vapour
- Ocean explosive eruption column
- Convective seawater circulation
- Hyaloclastite formation
- Pyroclastics & lavas
- Sheeted dykes

- Discharge
- Recharge

- Global cycling of elements + metals
- Alteration + Fe, Al, Ti-PSi, Ca, Na, K, Mg

- Proto-Pacific rift plume relaxation
- Time progression

- South Pole
- 60 N
- 20 N
- 40 N
- 20 S
- 40 S
- Equator

- ANS: Arabian-Nubian Shield
- EG: Eastern Ghats
- Eth: Ethiopia
- Mad: Madagascar
- NC: Napier Complex

- Laurentia magmatic province
- Pan-African Orogenic Belts

- Mawson continent
- Australia
- Congo
- Kalahari
- Siberia
- South China
- Rio Plata

- Mawson continent/Australia
- East African orogen
- West African & Brasilian orogen
- Iapetan rift
- Iapetus Ocean
- Laurentia magmatic province

- Laurentia magmatic province
- Pan-African Orogenic Belts
The image depicts a time-stratigraphic chart indicating major volcanic events and geological formations across different continental areas. Key geological features include:

- **At 780 Million Years Ago (Ma):**
  - Onset of Rodinia breakup
  - Transantarctic Mountains

- **At 750 Ma:**
  - Protracted breakup
  - Continental Flood Basalts

- **At 650 Ma:**
  - Opening of Iapetus

**Geological Formations and Events:**

- **Gaskiers**
  - Gairdner, Willouran
  - Franklin LIP

- **Marinoan**
  - Schaksberge/Chameis
  - Mwashia (Zambia)

- **Sturtian**
  - Cape Range Complex
  - Transantarctic Mts.

- **Kaigas**
  - Mackenzie Mtns.
  - Mt Harper Complex

**Geographic Areas:**

- **S. China dykes**
- **EL Beida, Fatira (Egypt)**
- **Arabian-Nubian Shield**
- **Laurentia**
- **S China**
- **North S. Wales**
- **Australia**
- **S China**
- **Laurentia**
- **Avalonia**
- **Amazonia**
- **Kalahari/Congo**
- **Antarctica**

**Key Features:**

- **Major volcanic events**
- **Extensive hyaloclastite**
- **Gl. diamictite overlying volcanics**
- **Age uncertainty**
a

annual dissolved riverine flux: 3.1e+10

volume of erupted hyaloclastite (m³ y⁻¹)

Flux of P to ocean (mol y⁻¹)

b

5-10x modern DRF

- Full simulation
- I: fully unzipped high
- II: fully unzipped moderate
- III: short ridge moderate

Modern dissolved riverine flux (DRF)