Global climate stabilisation by chemical weathering during the Hirnantian glaciation

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Abstract
Chemical weathering of silicate rocks is a primary drawdown mechanism of atmospheric carbon dioxide. The processes that affect weathering are therefore central in controlling global climate. A temperature-controlled “weathering thermostat” has long been proposed in stabilising long-term climate, but without definitive evidence from the geologic record. Here we use lithium isotopes (δ7Li) to assess the impact of silicate weathering across a significant climate–cooling period, the end-Ordovician Hirnantian glaciation (~445 Ma). We find a positive δ7Li excursion, suggestive of a silicate weathering decline. Using a coupled lithium–carbon model, we show that initiation of the glaciation was likely caused by declining CO2 degassing, which triggered abrupt global cooling, and much lower weathering rates. This lower CO2 drawdown during the glaciation allowed climatic recovery and deglaciation. Combined, the data and model provide support from the geological record for the operation of the weathering thermostat.

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Letter

The recovery and stabilisation of Earth’s climate system from perturbations is central to the continued survival of life. Chemical weathering of continental silicate rocks driving marine carbonate precipitation is the Earth’s primary long-term mechanism for removal of atmospheric CO2 (Berner, 2003). A temperature feedback control on weathering rates (i.e., greater temperatures cause higher weathering rates, removing more CO2) would result in a climate-stabilising mechanism. This “weathering thermostat” has long been postulated and assumed in models (Colbourn et al., 2015). However, direct evidence for weathering rate changes in response to climate perturbations has been harder to pin down in the geological record.

The Late Ordovician Hirnantian (~445 Ma) records the second largest mass extinction in Earth history. This was likely caused by rapidly decreasing temperatures, culminating in an ice-sheet over Gondwana (Elrick et al., 2013). As such, similarities exist between the Hirnantian and the Late Cenozoic glaciations (Ghiennie et al., 2014). The behaviour of atmospheric CO2 is of particular interest, because of the potential role of declining CO2 in initiating the glaciation and of increasing CO2 in terminating it (Vandenbroucke et al., 2010). Either or both could have involved changes in silicate weathering rates (Berner, 2003). The combination of changes in weathering rates and pCO2 also resulted in a global positive δ13C excursion (HICE) (Lenton et al., 2012; Ghiennie et al., 2014). Osmium isotopes have suggested a decline in weathering during the glacial maximum (Finlay et al., 2010). However, Os mainly traces weathering provenance, rather than weathering rates or processes. Lithium isotopes are the only tracer available whose behaviour is solely controlled by silicate weathering processes, and therefore give a unique insight into CO2 drawdown and climate-stabilisation.

Lithium isotopes (δ7Li) are not fractionated by biological processes (Pogge von Strandmann et al., 2016), and are not affected by carbonate weathering (Dellinger et al., 2015). The δ7Li of primary silicate rocks defines a narrow range (continental crust ~0.6 ± 0.6 ‰, basalt ~3–5 ‰; Sauzeat et al., 2015) compared to the high variability in modern rivers (2–44 ‰; Huh et al., 1998; Dellinger et al., 2015; Pogge von Strandmann and Henderson, 2015). Riverine values reflect weathering processes, particularly the extent of preferential uptake of Li into secondary minerals (Dellinger et al., 2015), and therefore reflect “weathering congruency”, defined as the ratio of primary rock dissolution (driving rivers to low, rock-like, δ7Li = congruent dissolution of rock), to secondary mineral formation (driving rivers to high δ7Li; Misra and Froelich, 2012; Pogge von Strandmann and Henderson, 2015). In modern oceans, rivers (~50 % of the ocean input, with a mean δ7Li ~23 ‰; Huh et al., 1998) are combined with mid-ocean ridge hydrothermal solutions (~50 %, with a mean δ7Li ~7 ‰; Chan et al., 1993). The oceanic sinks are incorporated into low-temperature clays in altered oceanic basalt (AOC) and marine authigenic clays (MAAC), which cumulatively impose oceanic sinks are incorporation into low-temperature clays in altered oceanic basalt (AOC) and marine authigenic clays (MAAC), which cumulatively impose

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Melchin et al., 2013) (see Supplementary Information for methods and data). The δ7Li values from all sections exhibit a positive excursion of ≤10 ‰ before the HIocene (Fig. 1). We rule out effects on carbonate δ7Li by silicate leaching, due to our processing technique (see Supplementary Information). We also rule out diagenesis, because trends and absolute values of δ7Li, δ13C and δ18O (Melchin et al., 2013) are reproduced in different sections, both bulk carbonates and brachiopods (Fig. 1). Overall, therefore, this suggests that the Li isotopic excursion represents a primary seawater signal.

While carbonates tend to be the usual seawater archive (e.g., Misra and Froelich, 2012; Pogge von Strandmann et al., 2013), silicates have also been investigated (Dellinger et al., 2017), and sediments older than Ordovician are considered to represent pre-depositional (unaltered by diagenesis) weathering signals (Li et al., 2016). Hence, detrital clays (which dominate at Dob’s Linn) should reflect changing local continental weathering conditions (see Supplementary Information and Fig. S-4). Tracers such as Si/Al, Li/Al or 187Os/188Os rule out control by changing provenance or clay mineralogy. Dob’s Linn exhibits an isotopic excursion of similar magnitude, but ~14 ‰ lower than the carbonates. While biostratigraphy suggests that the δ13C_carb and δ13C_erg of Anticosti and Dob’s Linn are slightly offset (Melchin et al., 2013) (Fig. 1), in all sections the relative timings of the δ7Li and HIocene are similar. Chemostratigraphy therefore suggests the Li isotope excursions occur contemporaneously (see Supplementary Information), consistent with lithium’s long modern ocean residence time (~1 Myr). A simple temperature dependence of the clay fractionation factor during weathering would only cause <1.6 ‰ variation (Li and West, 2014), and is therefore not the cause of the observed variability. Although shales, in particular clay fractionation factors, are under-constrained for a quantitative interpretation in isolation, their comparison to and temporal similarities with carbonates suggests a link.

Thus, global seawater compositions (represented by carbonates) appear to be responding to the same driving force as this local archive of continental weathering (represented by shales).

The pre- and post-excursion δ7Li_seawater values of ~15 ‰ are difficult to achieve in a modern ocean. It is likely that the AOC and MAAC sinks were broadly similar to today (Hazen et al., 2013), imparting an isotopic fractionation factor of ~15 ‰, which may be temperature-dependent, as discussed below. We do not consider a “sink-shift” between proportions of MAAC vs. AOC, as proposed for the Cenozoic (Li and West, 2014), because the Hirnantian duration is likely too short (1–2 Myr) for a transient change. Therefore, Li inputs must have had an isotope ratio close to 0 ‰. Assuming a modern-like hydrothermal input, this requires that rivers had δ7Li values essentially unfractonated from the continental crust (modern value ~0 ‰; Sasseet al., 2015). This possibility is supported by δ7Li values of ~2 ‰ for the Amazon river (Dellinger et al., 2015), and similarly low values during the peak of the Cenomanian-Turonian hyperthermal (Pogge von Strandmann et al., 2013). However, data here imply that Ordovician oceans were isotopically light at steady state. Given that the first non-vascular land plants were only just evolving and colonising the continents in the mid-late Ordovician (with associated organic acid production), it is probable that clay types were different and less abundant (Hazen et al., 2013). For example, illites, which cause little Li isotope fractionation (Millot and Girard, 2007), are thought to dominate prior to terrestrialisation by plants (Hazen et al., 2013). If this is a feature of early Earth weathering, then the continental crust’s δ7Li would have been mantle-like (~3 ‰), rather than driven isotopically light by weathering.

Assuming, therefore, that silicate weathering was highly congruent, we have created a dynamic non-steady state coupled Li and C cycle model (see Supplementary Information). In brief, the model uses Li formulations from previous work (Pogge von Strandmann et al., 2013; Lechler et al., 2015), with an added temperature dependence on the Li sink with a sensitivity of ~0.15‰/K (Li and West, 2014), and links the weathering flux to that calculated by the carbon cycle model (based on GEOCARB III). Existing climate models suggest that pCO2 needed to halve to ~8 PAL (present atmospheric level) to trigger the Hirnantian glaciation (Pohl et al., 2016). This could be initiated by a decline in degassing (McKenzie et al., 2016), an increase in plant cover (Lenton et al., 2012) or uplift (Kump et al., 1999), or a combination of these. A rather extreme decline in degassing from the initial Ordovician value of 1.5× to 0.75× modern causes CO2 to drop to ~6.5 PAL. Both the hydrothermal and riverine Li fluxes scale proportionally to degassing, resulting in no steady state change, but a transient adjustment of the oceanic Li reservoir causes a positive δ7Li excursion of ~3.5 ‰ (i.e. correct direction, but smaller excursion). In contrast, increasing plant-induced weathering (and associated clay mineral formation) causes a permanent, rather than transient δ7Li increase (see Supplementary Information), which is not observed in our data. However, it is possible that the two processes operated in conjunction. A 65 ‰ increase in uplift would create the same effect, but would be unprecedented in the Phanerozoic. Theoretically, the excursion could also be caused by...
an increase in riverine $\delta^7$Li by $\sim$15 ‰ with no change in flux. However this is unlikely, because it implies greater uptake into clay minerals, which would cause a decrease in river flux. This scenario also has no carbon cycle forcing, and hence we prefer a coupled flux and isotope ratio change, initiated by a degassing change.

A recent insight is that a glacial “tipping point” existed in the Late Ordovician, where, once global temperature dropped to a critical threshold, northern high latitude sea-ice expanded abruptly, causing a further decrease in global temperatures and rapid expansion of an ice sheet on the Southern polar land surfaces (Pohl et al., 2016). These ice albedo and heat transport feedbacks operate far faster than the long-term carbon cycle. Hence to represent this we implement an abrupt cooling when CO$_2$ reaches $\sim$8 PAL, generating reduced silicate weathering rates. To prevent an immediate abrupt warming, we assume some bi-stability of temperature and ice cover such that CO$_2$ has to rise to $\sim$8 PAL before deglaciation occurs. The cooling-induced reduction in global weathering flux (by $\sim$4×), causes an accelerated rise in $\delta^7$Li from 17–19 ‰ (depending on continental crust composition) to $\geq$25 ‰ (Fig. 2), which is reversed when the build-up of CO$_2$ triggers abrupt warming and deglaciation. Hence peak $\delta^7$Li is predicted to be at the end of the glacial interval, consistent with sea-level reconstructions (Fig. 2). The size of the excursion could be increased by coupling the weathering decline with higher riverine $\delta^7$Li, as suggested by the shale record (Fig. 2). This could be caused by an increase in the continental residence time of water allowing more clay formation, or a temperature-dependent shift in clay mineralogy. Such a change in congruency could also assist a vegetation-accelerated scenario, where terrestrialisation enhanced weathering, but enhanced glacial grinding forced a return to more congruent weathering. Such vegetative forcing would also cause a transient $\delta^7$Li excursion (Fig. S-9), albeit one of longer duration, hence we consider this less likely. Critically, the model can explain an increase in $\delta^7$Li as cooling starts, but before the full glaciation was initiated, and the highest oceanic $\delta^7$Li occurring at the end of the glaciation as observed in the record. $^{187}$Os/$^{188}$Os values (Finlay et al., 2010) agree with this scenario, suggesting inhibition of weathering by cooling (which would also increase CO$_2$; Kump et al., 1999) and hence a change in provenance focus, coincident with the $\delta^7$Li peak. Our model also predicts $^{86}$Sr/$^{88}$Sr variation within the observed scatter (Shields et al., 2003), lending further credence to our interpretation (see Supplementary Information).

The data and model are therefore consistent with the Hirnantian glaciation being initiated by declining CO$_2$ degassing, leading to a transient decline in silicate weathering, in turn causing an atmospheric CO$_2$ increase that ultimately terminated the glaciation. The Hirnantian has been compared to Cenozoic glaciations (Ghiennie et al., 2014), where both periods are now characterised by increasing $\delta^7$Li values (Misra and Froelich, 2012). The positive $\delta^7$Li excursion during the Hirnantian cooling event also compares well to negative $\delta^7$Li excursions during warming events (Pogge von Strandmann et al., 2013; Lechler et al., 2015). Overall, therefore, this study shows that if a tectonic-driven climate control (degassing) can push the climate system out of balance, a temperature-dependent feedback via silicate weathering will eventually stabilise the climate. Such a weathering thermostat has frequently been postulated as a climate regulating process, but has proven remarkably difficult to unambiguously demonstrate in the geological record.

![Figure 2](image)

**Figure 2** Comparison of data and model results. Sea level timing is from stratigraphic data (Ghiennie et al., 2014). Seawater Li isotope data were generated from carbonate data by adding a 4 ‰ fractionation factor (Marriott et al., 2004). The model shows the changes in riverine and hydrothermal Li fluxes, the pCO$_2$ levels and temperature anomalies caused by these changes, and the resulting oceanic $\delta^7$Li curve. The red model lines are for scenarios where riverine $\delta^7$Li = 3 ‰, 0 ‰, a change from 0 to 10 ‰ during the glaciation and “shale-constrained” (s.c.), using Dob’s Linn $\delta^7$Li data to constrain river values (see text and Supplementary Information for detail).

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**Author Contributions**

PPvS wrote the research proposal, carried out the analyses and wrote the manuscript. TML and PPvS conducted the modelling. AD, AJF and DS provided samples, geochemical context and edited the manuscript. MJM assisted in analyses and edited the manuscript.


