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Evaluating the role of large igneous provinces (LIPs) and the slow carbon cycle in the formation of the first Snowball Earth glaciation, the Sturtian

A report submitted as the examined component of the Project Module SXG390

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Topic Area: Past Environmental Change

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Acknowledgements and dedication

The author would like to acknowledge the help and support of her tutor

As ever the four 'M's were of vital emotional support

This report is dedicated to Stuart Gibson.

Abstract

At the end of the Neoproterozoic, the Earth became 'Snowball Earth'. Global temperatures from pole to tropics dropped below freezing twice for millions of years at a time, each glacial interval separated by a period where global temperatures exceeded 40°C. The reasons for these drastic climatic variations are not well understood. Reviewing recent literature, this paper explores a potential contributing factor, the actions of the slow carbon cycle during and after the emplacement of large igneous provinces (LIP) in the late Tonian. The paper considers recent work in relative and absolute dating of the rock record in the late Tonian as it has provided evidence for key events. Absolute dating on igneous rocks co-existing with glacial tillites date the onset of the first glaciation at 717 million years ago. During the late Tonian the continents were in the process of breaking apart from the super continent Rodina. This resulted in the emplacement of several large igneous provinces (LIPs) including the Franklin whose presence coincides with large perturbations in carbon isotope values also seen at this time. Strontium, Neodymium and Osmium isotope ratios appear to suggest increases in silicates weathering. Outgassing and silicate weathering may contribute to rising and lowering CO₂ levels respectively. The location of LIPs at the tropics in warm conditions may mean that weathering rates may have increased enough to ensure or contribute to enough CO₂ drawdown to cool the Earth. However, how outgassing and the global temperature interact before Snowball onset are unknown. Implications for future climate change for the Earth are unclear, total solar insolation (TSI) and albedo are major forcing agents for climate and TSI was 94% of present values in the Tonian. However, the Cryogenian was preceded by 1 Gy of stable climate, so other factors such as silicate weathering may still be important.

Word count: 300

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Chapter 1 - Introduction

1.1 Introduction

The Cryogenic Period in the Neoproterozoic was characterised by at least two major global glacial events, the Sturtian at 717 – 635 Mya, lasting approx. 60 my and the Marinoan at 645 – 640 mya, lasting around 5 mya. (Rooney et al, 2015). During these events the Earth was cold enough for glacial tillites to be deposited at equatorial latitudes, and it became the 'Snowball Earth' (Knoll, 2015).

There is debate about the cause of the 'Snowball Earth'. However, most researchers accept that Earth entered a climate state called the 'runaway albedo'. If glaciations extend to 30° N/S of the equator, positive feedback forms between albedo, ice cover and global temperatures and a Snowball Earth condition becomes inevitable (Schrag et al, 2002). Whether the Earth was fully glaciated (hard snowball) or partially glaciated (soft/slushball) is contended. However, both involved glaciation at low latitudes so this report does not delineate between the two. For more discussion about hard/soft snowballs see Young (2021).

Arnscheidt and Rothman (2020) developed a model where a planet can become a 'snowball' using the parameters of solar radiation, runaway ice-albedo effect, and the actions of the 'slow' global carbon cycle. The slow carbon cycle is thought to regulate global climate by the antagonistic processes of volcanic degassing (increases atmospheric CO₂) and silicate weathering (decreases CO₂). This report explores how slow carbon cycle processes may have contributed to the initiation of global glaciation.

The Cryogenian was preceded by the late Tonian. During this time several large igneous provinces (LIPs) were emplaced (Cox et al, 2016). LIPs are defined as large (over 0.1 M km³) intra-plate emplacements of usually mafic material. They are emplaced over a relatively short period of time, usually less than 5 million years (Ernst and Youbi, 2017). The presence of LIPs throughout the geological record have been associated with climate and biological perturbation such as mass extinctions. (Ernst and Youbi, 2017). LIPs can affect CO₂ outgassing and silicate weathering rates. Exploration of the role of the slow carbon cycle cannot be considered without also exploring the contribution of LIPs to initiation of the Sturtian glaciation.

1.2 Scope

After considering work carried out to date events in the late Tonian, the report will focus on the actions of the global slow carbon cycle evidenced through key isotope systems. The paper will attempt to ascertain the contribution of outgassing and silicate weathering to carbon dioxide levels and climate during and after the emplacement of LIPs. The potential for future Snowball Earths will also be explored.

1.3 Objectives

The objectives of the report are to:

1. Review work around dating of key events in the late Tonian, including the start of the Sturtian glaciation.

2. Using chemostratigraphy analyse and evaluate evidence for the actions of the slow carbon cycle in global climate change
3. Evaluate the climate forcing potential of LIPs and related slow carbon cycle activity
4. Determine the potential of LIPs and associated carbon cycle behaviours and changes for future climate change on Earth

1.4 Methodology

Searches for material were conducted using several tools including the OU Library Search, Google Scholar and connectedpapers.com. Reverse and forward citation searches were used from key papers such as Schrag et al (2002) to try to identify updated work and bibliographies from papers were also mined.

Chapter 2 – Dating the late Tonian

Key questions around formation of Snowball Earth cannot be answered without accurate dating (Macdonald et al, 2010). There are two types of dating - relative dating and absolute dating. The two methods work together to construct the geological time scale.

2.1 Relative dating: chemostratigraphy

Relative dating of the Tonian is a challenge. Conventional relative dating techniques used in Phanerozoic rocks rely heavily on biostratigraphy, i.e., using taxonomic relationships between fossilised organisms to determine relative dates between different rock units. Complex life had not evolved in the Neoproterozoic meaning there is a lack of hard-body parts for detailed fossil identification. Although Vase Shaped Micro-organisms (VSMs) are starting to be used to date Tonian strata, taxonomical knowledge about these organisms is still developing, meaning precise dating is not possible (Riedman et al, 2018). Therefore, chemostratigraphy is accepted as being the most useful method for relative dating for the late Tonian. (Halverson et al, 2020).

Chemostratigraphy allows geochemical information recorded in rock units separated geographically to be correlated with each other and relatively dated. The data collected can also be used for other purposes (see chapter 3). Carbon and Strontium isotopes have commonly been used in dating studies.

Figure 2.1 (taken from Halverson et al, 2020 and 2022), shows how $\delta^{13}\text{C}_{\text{carb}}$ values have been plotted for rock units from two different locations. Broad patterns in isotope variations can be discerned and these then allow the different rock units to be correlated.

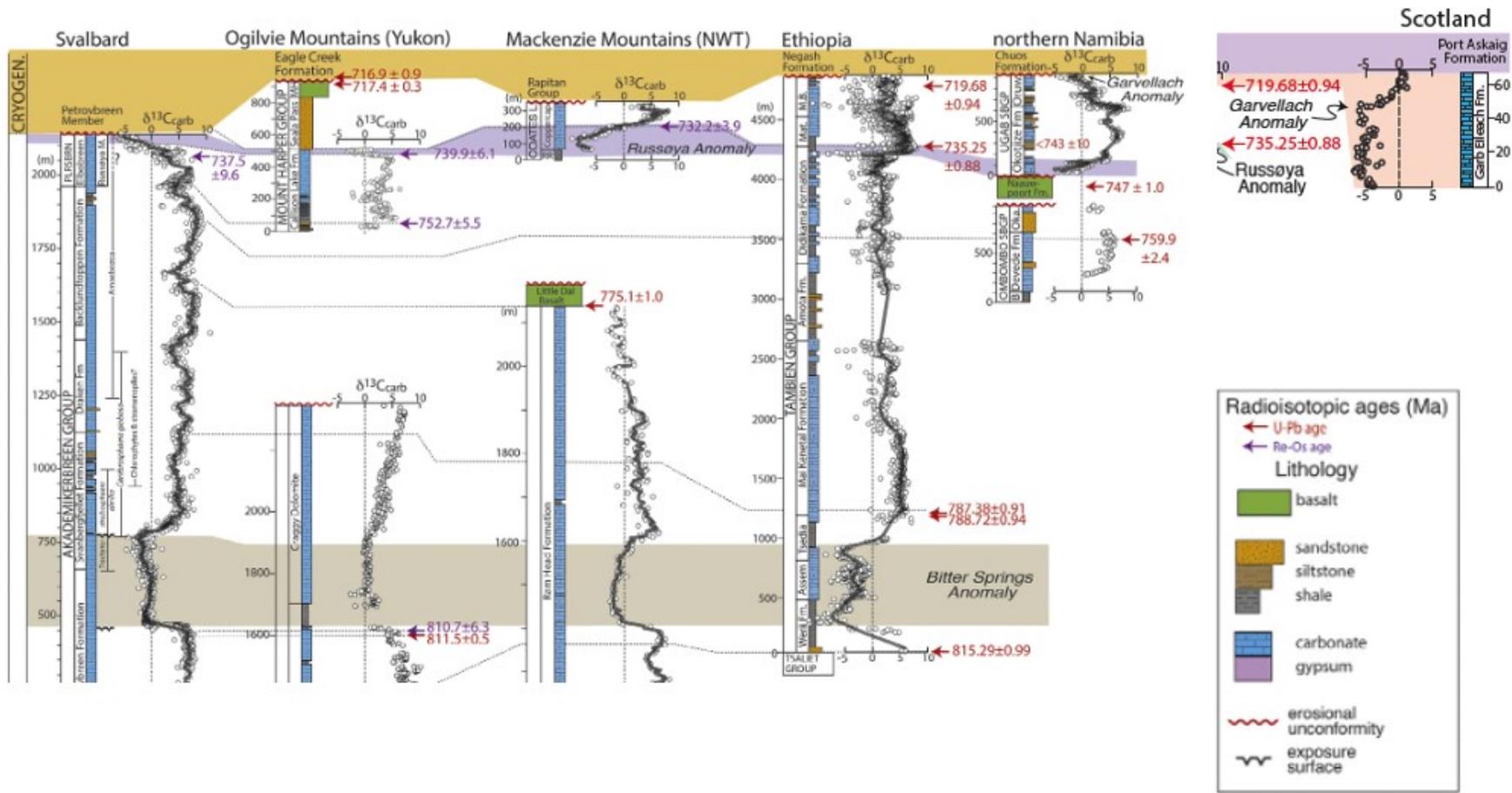


Figure 2.1 Amalgam of figure 17.4 from Halverson et al (2020) (Scotland data) and figure 3 from Halverson et al (2022) showing succession of late Tonian sediments from the Bitter Spring Anomaly onwards to the start of the Sturtian for 6 locations. It also shows $\delta^{13}C_{carb}$ data and radioisotopic ages for 6 locations. Note that the 'vertical axis' is not date but thickness of strata, illustrating the continuing issues of dating these sedimentary rocks. Thickness of strata will also be determined by deposition rates, and this will differ between localities. The only constrained dating information is obtained from the U-Pb/Re-Os systems

Issues can arise with correlating data from sediment beds across different locations. For example, assumptions about rates of sediment deposition between locations may be incorrect and dating uncertainties can be poorly constrained or large (Halverson et al, 2022).

Another major issue regarding the use of isotopes and stratigraphy is determining whether a particular isotope signal has been caused by local processes, such as diagenesis or has a global cause. Hoffman and LaMonthe (2019) found that ^{13}C varied considerably between rock units in one area (Otavi, Namibia) - so some changes can be due to local processes. Correlation between rock units as seen in Figure 2.1 is therefore important to verify the presence or absence of a global isotope anomaly as only this can allow dating.

2.2 Absolute dating

Absolute dating with radiogenic isotopes systems is impossible in sedimentary rocks because isotope decay system values are not 'locked in' at the date of deposition but at the date of formation of the clasts that make up in parent rock. However, igneous rocks can be dated accurately, and they are very useful in providing absolute dating if they crosscut, underpin or overlay sedimentary successions of interest. The late Tonian LIPs have been very useful in terms of providing accurate dates. (Ernst et al 2008).

Macdonald et al (2010), dated zircons in a composite tuff/glacial deposit in Canada using the U-Pb isotope system. The tuff was thought to be from the Franklin Large Igneous Province emplaced at tropical latitudes determined by palaeomagnetism. The resulting date - 716.47 ± 0.24 Ma has been accepted by most studies as being the date of Sturtian onset. Several other studies from Oman and South China also corroborate this date (see table 1 in Hoffman et al, 2017). This gives a date for the start of the Sturtian glaciation and this is the date that is used in more recent studies (e.g., Cox et al, 2016; Hoffman et al, 2017; Halverson et al, 2020).

2.3 Discussion: a timeline of activity and setting the scene

Figure 2.2 summarises some of the notable geochemical and geological events and their dates discovered so far in the late Tonian. The data is rendered to approximations, but the diagram show how these events temporally relate to each other, suggesting correlation. This has allowed hypotheses to be formed about underlying causative processes. These processes in relation to LIP emplacement and isotope values are explored in Chapter 3.

IMAGE REDACTED FOR COPYRIGHT REASONS

Figure 2.2 amalgamating LIP timing and indications of relevant volume from figure 2 Cox et al (2016), Sr ratios from Chen et al (2021), $\delta^{13}\text{C}_{\text{carb}}$ values and paleogeography extracted from figure 1 from Tang et al (2022). All data is approximate.

Chapter 3 – using isotope systems to determine slow carbon cycle activity and extent of silicate weathering

Carbon and Strontium isotopes are commonly used to determine slow carbon cycle activity. However, this section also discusses two studies that used the Neodymium and Osmium isotope system to obtain more defined details about the nature of silicate weathering.

It should be noted that isotope systems discussed here describe generic carbon cycle action and silicate weathering only. No isotope data was found in the literature for outgassing.

3.1 Carbon isotopes ($\delta^{13}\text{C}_{\text{carb}}$)

The carbon isotope system uses the ratio ($\delta^{13}\text{C}$ value) between two stable isotopes - the most common ^{12}C and the rarer ^{13}C . As they have different atomic masses they fractionate differently. For example, photosynthesis prefers to use the lighter isotope ^{12}C when fixing CO_2 . This sequesters ^{12}C in organic carbon leaving a higher ratio of ^{13}C in the atmosphere and oceans to form carbonates. (Rollinson and Pease, 2021a).

Fractionation of this kind results in $\delta^{13}\text{C}$ values for two reservoirs of carbon in the oceans that contribute to sediments, organic ($\delta^{13}\text{C}_{\text{org}}$) and inorganic i.e. carbonate ($\delta^{13}\text{C}_{\text{carb}}$) values. The two reservoirs are assumed to co-vary although there is evidence that the relationship had de-coupled in the Neoproterozoic (Johansson et al, 2018). $\delta^{13}\text{C}_{\text{carb}}$ values are used as they are more reliable than $\delta^{13}\text{C}_{\text{org}}$ because of concerns of secondary alteration and contamination (Johansson et al, 2018)

For much of the Proterozoic, $\delta^{13}\text{C}_{\text{carb}}$ values were neither very positive nor negative (ranging from -2‰ to $+2\text{‰}$) suggesting that the climate was stable (Hoffman et al, 2021). The term 'Boring Billion' has been used to describe the 1 billion years pre-dating the late Tonian.

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Figure 3.1 diagram showing $\delta^{13}\text{C}_{\text{carb}}$ values compared to VPDB standard, from the Archean through to the start of the Phanerozoic. The diagram includes the postulated date range for the Great Oxidation Event (GOE). Thereafter from approximately 2.0 Gya to 900 mya carbon isotope values were relatively stable. (adapted from Hoffman et al, 2021). Dates of major negative carbon isotope excursions (CIEs) identified in dating are labelled by the author.

Figure 3.1 shows that from the late Tonian onwards (approximately 820 my) starting with the Bitter Springs Anomaly (Hoffman et al, 2021), $\delta^{13}\text{C}_{\text{carb}}$ values start to fluctuate, rising to positive values at around 8 ‰ with punctuations of negative values ranging from -2 to -6 ‰. The three most important negative carbon isotope excursions (CIEs) identified during dating are labelled in figure 3.1. These perturbations continue throughout the Cryogenian and Ediacaran before settling down again in the Cambrian. After this they remain at elevated positive levels compared to the 'Boring Billion' but do not reach substantial negative values.

3.2 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope system

$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios (with some constraints around diagenesis and secondary alteration of sediments (Park et al, 2019)) can detect whether sediment sources have resulted from weathering of continental rocks or from mantle sources. Weathering from continental rocks and riverine sources tends to generate a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio whereas material from mantle sources result in lower ratios (Rollinson and Pease, 2021b). There is evidence from a few papers including Fairchild et al (2018) that suggests that the Sr ratio decreased to 0.7064 just before the start of the Sturtian glaciation. Rooney et al (2014) also found a decrease in Sr ratio to 0.7064 which is also consistent with values obtained from Cox et al (2016).

3.3 $^{187}\text{Os}/^{188}\text{Os}$ isotope system

^{187}Os is produced by β decay of ^{187}Re . In crustal rocks this results in high $^{187}\text{Os}/^{186}\text{Os}$ ratios. The $^{187}\text{Re}/^{186}\text{Os}$ ratio is lower in mafic and ultramafic rocks and therefore the Os ratio value may be able to determine whether a weathering source is mafic. (Dickson et al, 2021). Additionally, ^{187}Os has a relatively short residence time in the oceans meaning it can be used for fine-grained analysis of dating of emplacement, weathering rates and climatic effects, i.e. it can detect the presence of weathered young crust (Rooney et al, 2014). Rooney et al (2014) measured $^{187}\text{Os}/^{188}\text{Os}$ values for pre-Cryogenic sediments and found values comparable to mantle ratios.

3.4 Neodymium (Nd) isotopes

Cox et al (2016) measured Nd isotope ratios in mudstones that were deposited in basins near to Neoproterozoic large igneous provinces (LIPs) from a number of locations across the globe. Geochemical evidence of surface weathering of LIPs should be detected preserved as a particular Nd isotope ratio. Weathered material from mantle sources should show a high $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (also called the ϵ_{Nd} value), whereas continental crust sources would show a low ratio. (Rollinson and Pease, 2021b)

ϵ_{Nd} values are unaffected by subsequent processes such as sedimentation and metamorphism (Rollinson and Pease, 2021b) so it is a robust proxy for the presence or absence of mantle material at time of weathering. Cox et al (2016) showed high ϵ_{Nd} values across several locations just before the onset of the Sturtian.

3.5 Discussion

Most primary research papers that measured $\delta^{13}\text{C}_{\text{carb}}$ values note only that it underwent significant perturbations (see for example Fairchild et al, 2018; Halverson et al, 2018 and

2022). $\delta^{13}\text{C}_{\text{carb}}$ values and carbon cycle activity are more commonly discussed in modelling studies and reviews.

Godderis et al (2011)'s review of modelling papers speculates that negative $\delta^{13}\text{C}_{\text{carb}}$ values in the Tonian are caused by a depletion in the partial pressure of CO_2 in the atmosphere ($p\text{CO}_2$). Black and Gibson (2019) suggest that negative $\delta^{13}\text{C}_{\text{carb}}$ values could be caused by an injection of mantle material into the carbon cycle, such as from LIP emplacement. However, mantle $\delta^{13}\text{C}$ values are around -5‰ meaning that a -6‰ CIE (as in the Russøya event) could not be accounted for by an influx of mantle ^{13}C alone. Other processes would have to operate e.g. an increase in primary productivity. (Cox et al, 2016; Gernon et al, 2016) or a flux of methane (Godderis et al, 2011).

Apart from speculation about input of mantle material, it would seem that $\delta^{13}\text{C}$ values are not particularly useful for determining slow carbon cycle activity *per se*. They are useful for determining the overall activity of the carbon cycle. Black and Gibson (2019) consider that determining carbon isotope composition of LIP outgassing is an important area of future work, this might increase the usefulness of carbon isotopes for the slow carbon cycle.

The lowering of the Sr ratio to around 0.7064 shown by multiple studies in the lead up to the Sturtian seems to suggest an increased input of sediment derived from mantle sources. This could be caused by increased silicate weathering of the Franklin LIP. The use of Nd and Os isotopes by Cox et al (2016) and Rooney et al (2014) respectively, offer a finer level of detail about the source of weathering – both indicate increased weathering from young mafic sources. However, more studies will need to be carried out to determine if these isotope values can be found elsewhere and how these changed over time.

Chapter 4 – Large Igneous Emplacements in the Tonian and effects on the slow carbon cycle

This section will attempt to explain potential climatic effects of silicate weathering and outgassing of LIPs, particularly the Franklin LIP. This is the largest Tonian LIP emplaced and coincides with the date of Sturtian glacial initiation (Macdonald et al, 2010).

4.1 Silicate weathering and $p\text{CO}_2$ levels

4.1.1 The silicate weathering process

Silicate weathering results in a net drawdown of CO_2 from the atmosphere as can be seen by the chemical equations given in figure 4.2 below. It is important to emphasise that only silicate weathering acts in this way as carbonate weathering does not. This net drawdown results in a reduction in $p\text{CO}_2$ (Cockell et al, 2007).

IMAGE REDACTED FOR COPYRIGHT REASONS

Figure 4.1: diagram from Cockell et al (2007) showing chemical equations associated with carbonate and silicate weathering. Only silicate weathering results in a net draw-down of CO₂

4.2.2 Silicate weathering and climate

Godderis et al (2003) attempted to quantify parameters that might lead to glaciation from silicate weathering of a basaltic LIP using late Tonian values for solar flux (94% of present-day value) and albedo. The model predicted that if starting pCO₂ was in the range of 208 ppmv (global temperature of 0.8 °C) a LIP with an area of 6 × 10⁶ km² emplaced at tropical latitudes, undergoing silicate weathering would initiate a global glaciation. This would cause pCO₂ levels to drop to below 135 ppmv

This study has not found any work that tests links between the Franklin LIP's weathering rates and either pCO₂ or climate change, so two studies involving Phanerozoic LIPs have been used as analogues. Both LIPs are basaltic in composition – basaltic (mafic and ultramafic) rocks weather faster than granitic rocks (Dessert et al, 2003; Ernst and Youbi, 2017). The results are shown in table 4.1 alongside Godderis et al's model and data for the Franklin LIP.

LIP	*Surface area/Mm ²	*Date/Mya	Latitude of emplacement	pCO ₂ fall	Estimated temperature drop/°C	Study
Godderis et al model	6.0	n/a	Lower latitudes	73 ppmv	Not given but starting temperature is 0.8 °C	Godderis et al (2003)
Franklin	2.62 (original), 0.04 (present day)	720	Lower latitudes	Not known	Not known	n/a
Deccan Traps	0.83 (original), 0.56 (present day)	66	Partly equatorial	In the region of 20%	0.55	Dessert et al (2001)

Siberian Traps	3.46 (original), 0.47 (present day)	252	Mid-high latitudes	By 746 ppmv	1.07	Grard et al (2005)
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*Data from Park et al (2021), table 7.1

Table 4.1: table of key data from Dessert et al (2001), Godderis et al (2003) and Grard et al (2005) combined with data from Park et al (2021) on LIP weathering and effects on pCO₂ and climate

It would seem possible that silicate weathering of the Franklin could cause a drop in global temperature of 1 – 2 °C. Whether that would result in global glaciation would depend on the global temperature pre-emplacment.

4.2.3 Silicate weathering of LIPs and palaeolatitude

Dessert et al (2001) determined that temperature and run-off are the biggest constraint on silicate weathering rates for basaltic material. It has been suggested that emplacement of the Franklin (LIP) on the equator may have resulted in higher silicate weathering rates as both temperature and run-off rates are higher at low latitudes. These higher weathering rates may result in higher CO₂ draw-down. (Johansson et al, 2018).

Johansson et al, 2018 analysed LIPs emplaced from 400 mya to the present day by comparing LIP area and proxy pCO₂ values. They found increased CO₂ drawdown from LIPs positioned in the 'humid zone'- a region between 5 – 15° N/S of the equator. However, Johansson et al's methodology was questioned by Park et al (2021) who noted issues with constraining pCO₂ values due to calibration issues and the effects of potential secondary alteration. Using a methodology that compared LIP emplacement area to global glaciation latitude for LIPs in the Phanerozoic (but including the Franklin) Park et al (2021) found no relationship between emplacement of LIPs at tropical latitudes and the extent of global ice sheets. Although the two studies may appear to contradict each other, they examine different relationships between LIP area: Johansson et al (2018) pCO₂ and Park et al (2021) the global glaciation extent. At best it could be concluded that the link between latitude of LIP weathering, pCO₂ and global glaciations is not a simple one. In addition, if pre-glacial global temperatures are low as indicated in Godderis et al (2003)'s model then what effect this would have on silicate weathering rates is unclear.

4.2 The effects of LIP outgassing on pCO₂ levels

Calculating the degree of CO₂ outgassing from a LIP is problematic for several reasons. Carbon dioxide is directly outgassed in volcanic eruptions, but the gas can travel to the atmosphere through the crust (Armstrong Mackay et al 2014) making it difficult to determine the time scales for outgassing. There are no current LIPs being emplaced at present that would allow direct measurement of CO₂ outgassing. CO₂ quickly exsolves from magma meaning geochemical evidence from historical LIPs may not be reliable. (Jones et al, 2016)

It is possible to use incompatible elements that are not outgassed such as Barium (Ba) and Niobium (Nb) whose behaviour closely mimics CO₂. Reporting from two studies using that approach, Black and Gibson (2019) found that the degree of variability in carbon content in LIPs varied considerably from 0.1 and 2 wt% CO₂.

CO₂ outgassing rates are also very variable and depend on many factors such emplacement rate, sources of magma, the extent to which the LIP is under or above water and whether

magma interacts with crustal rocks causing melting, metamorphism, and further outgassing (Ernst and Youbi, 2017).

There have been no modelling studies carried out on climatic effects of outgassing from the late Tonian LIPs and again work carried out with other LIPs are used as analogues.

Self et al (2006) modelled the extent of CO₂ outgassing from a theoretical continental flood basalt eruption. CO₂ is highly insoluble in basaltic melts and the study assumed a 100% degassing rate. The model resulted in a value of 0.5 wt% CO₂ for the magma. This corresponds to an estimate of the amount of CO₂ released of 1.4×10^{14} kg per km³ which contributes a small fraction to the total amount of CO₂ in the atmospheric reservoir. When considering a basaltic emplacement alone Ganino and Arndt (2009) agreed that the volume of CO₂ released would not be large compared to the atmospheric reservoir, unless the LIP was emplaced into sedimentary rocks, such as carbonates. This may increase CO₂ outgassing through metamorphism. CO₂ through metamorphic outgassing is explored in Landwehrs et al (2020) for the Central Atlantic Magmatic Province (CAMP) where CO₂ released is modelled at 2500 – 7500 GtC over pulses lasting 1 – 6 kya. This causes a global temperature rise of between 1.8 – 4.4 °C. Dessert et al (2001) estimated that the Deccan eruptions resulted at first in warming of the atmosphere of 4°C due to CO₂ outgassing.

4.4 Discussion

Over shorter timescales, outgassing produces substantially higher temperature increases than silicate weathering, but the timescales these processes operate over are crucial. Both Dessert et al (2001) and Godderis et al (2003) show an increase in *p*CO₂ and global temperatures (up to 4 °C) caused by outgassing shortly after LIP emplacement. These figures are supported by Self et al (2006) and Ganino and Arndt (2009). However, outgassing acts over timescales in the region of thousands of years. After this time period, temperature and *p*CO₂ drop due to silicate weathering over a longer timescale resulting in a global temperature drop below pre-LIP value. These might be small temperature drops (0.55 °C for Dessert et al (2001), 1.1 °C (Grard et al, 2005)) but the actions of silicate weathering operate over a longer timescale, 10⁵ – 10⁶ years (Mackenzie and Jiang, 2019) compared to outgassing. Silicate weathering would appear to draw down more CO₂ over time than CO₂ is outgassed into the atmosphere (Johansson et al, 2018). In addition, the rise of temperatures associated with outgassing would also raise the rate of silicate weathering. Interplay between outgassing and silicate weathering and the effects on climate is not yet fully understood.

Park et al (2021) concluded that it was unlikely that emplacement of a LIP in the humid zone could cause enough silicate weathering to result in global glaciation, although others disagree (Godderis et al, 2003; Cox et al, 2016). Park et al (2021) also suggests other events such as the formation of arc-terranes and the release of SO₂ aerosols may also have contributed to global cooling. Macdonald and Wordsworth (2017) postulate that sulfur aerosols outgassed from LIPs may have blocked solar radiation enhancing the Earth's albedo and causing cooling. However, this cooling effect operates over a very short timescale – in the region of years (Ernst and Youbi, 2017).

Horton, (2015) suggests that basaltic weathering elevates phosphorous levels in the ocean leading to increased primary productivity. This could draw down more CO₂ and produce the negative δ¹³C_{carb} values seen in the late Tonian. If *p*CO₂ was already at low levels in the atmosphere this could also contribute to global cooling.

The contribution of these factors to Snowball initiation cannot be ascertained without better evidence of late Tonian global temperatures and *p*CO₂. If global temperatures were low then only small drops in temperature due to LIP weathering would have resulted in global

glaciation. However, that is not known at present. MacLennan et al (2020) determined that glacial deposits interbedded with igneous rocks were deposited at tropical latitudes around 751 Mya (the igneous rocks allowed the glacial deposits to be dated) inferring very cold surface temperatures.

Chapter 5 – implications for future climate change on Earth

There have been several LIP emplacements in the Phanerozoic whose timing associates them with large scale extinction events (Ernst and Youbi, 2017). The Earth has also been in greenhouse and ice-house states since the Neoproterozoic, but ice-house conditions with permanent ice caps have not rivalled the extreme climatic conditions of the Cryogenian.

This section briefly discusses some other factors that may need to be considered when evaluating the potential for future Snowball Earths.

5.1 Albedo

One parameter that features in Godderis et al's (2003) and Arnscheidt and Rothman's (2020) models is continental albedo. Albedo is a complex parameter involving cloud cover, reflectivity of ice and snow, continental cover and paleogeography. This paper cannot examine these in detail, but it is worth considering continental albedo as this differed in the Neoproterozoic.

The continents in the late Tonian were denuded of plant life. Estimates of albedo vary, some authors use a value nearer to that of deserts (0.27 to 0.35) whereas one modelling study preferred to use an albedo like Mars at around 0.17 (Spiegel et al, 2015). The Earth's average albedo is 0.3 at present ((Pierrehumbert et al, 2011) Land plants decrease albedo (Li et al, 2018). However, Spiegel et al's (2015) extensive modelling show that it was almost impossible to create a Snowball Earth if albedo was lower than 0.27 unless $p\text{CO}_2$ was also very low.

5.2 Solar insolation

Solar flux was 96% of today's values in the Neoproterozoic (Hoffman and Schrag, (2002); Godderis et al (2003); Pierrehumbert et al (2011)). This may have resulted in a decrease in flux by 14 W m^{-2} compared to today's values. A decrease in solar flux of 0.5 W m^{-2} results in a temperature drop of around 7°C . (Pierrehumbert et al, 2011). Pierrehumbert et al (2011) calculate that to maintain surface temperatures at today's values, the Neoproterozoic would require a $p\text{CO}_2$ value of around 12 times pre-industrial values, assuming the lack of action of other greenhouse gases such as methane. Spiegel et al (2015)'s modelling also show total solar insolation (TSI) to be a major forcing agent for Snowball initiation. A reduction of TSI to 94% of today's values always produced a Snowball even if $p\text{CO}_2$ levels were high and albedo was low.

5.3 Discussion

It could be concluded that the potential for a Snowball to form on Earth in the future is unlikely due to the large forcing effects of TSI and albedo and the changes seen in these since the Tonian. However, the presence of the "Boring Billion" preceding the Cryogenian with its stable carbon isotope values confounds that conclusion. TSI was 94% (perhaps even

lower) during that time and there were no global glaciations. There must have been other factors at work. The concept that slow carbon cycle activity through LIP emplacement was a contributing factor to the creation of the original Snowball Earth is reasonable although the potential for outgassing and silicate weathering to form future Snowballs is uncertain given current TSI and albedo.

Chapter 6 – Conclusions

6.1 Key conclusions

- Evidence collected for dating shows that the late Tonian (820 – 717 Mya) was characterised by the emplacement of several large igneous provinces, including the largest, the Franklin, just before the start of the Sturtian glaciation. Variations in $\delta^{13}\text{C}_{\text{carb}}$ values are also seen along with a gradual reduction in Sr isotope ratios.
- The reasons for the $\delta^{13}\text{C}_{\text{carb}}$ variations are not fully understood but it is generally accepted they are a result of perturbations in the carbon cycle. How these might relate to the slow carbon cycle and LIPs is not clear, but one suggestion is an input of depleted ^{13}C from the mantle via outgassing
- Reductions in Sr isotope ratios suggest increased input from mantle material into sediments through weathering. Results from more precise isotope systems (Nd and Os) suggest that the weathered material originates from young, basaltic material such as LIPs. However, there needs to be more work to replicate results and correlate from other rock units elsewhere.
- Modelling studies show LIP emplacement drives higher temperature increases over short timescales followed by a net smaller reduction in temperature caused by silicate weathering. Whether this could initiate global glaciation might depend on the global temperature at onset. This is not known.
- Silicate weathering rate is largely defined by temperature and run-off rate. This suggests that the Franklin emplacement at the equator would increase weathering rate, having consequences for CO_2 drawdown and glaciation. However, if global temperatures were very low even at the equator the effects on weathering rate are not known.
- TSI and albedo are major forcing agents for global glaciation. In the late Tonian, TSI was 94% of present value and albedo may have been higher. However, despite this, the billion years preceding the Cryogenian glaciations were remarkably stable. This suggests that some other factor may have been at play. This may have been LIP emplacement and weathering as these are temporally correlated to changes in $\delta^{13}\text{C}_{\text{carb}}$ values although the causative link between the two requires to be found.

6.2 Future work

More work should be carried out to determine the causes of the $\delta^{13}\text{C}_{\text{carb}}$ variations at the end of the Tonian and how these might relate to the slow carbon cycle. How outgassing contributes to carbon isotope values could be clarified – could LIP outgassing cause negative $\delta^{13}\text{C}_{\text{carb}}$? There could be more modelling carried out on late Tonian LIPs to

constrain the relationships between silicate weathering, pCO₂ and global climate – does the sequential emplacement of several LIPs cause a progressive decrease in temperature? Developing a reliable paleothermometer would also help determine global temperatures in the lead up to the Cryogenian.

Word count: 4931

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