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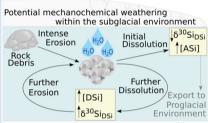
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Physical weathering by glaciers enhances silicon mobilisation and isotopic fractionation

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Abstract



Glacial meltwaters export substantial quantities of dissolved and dissolvable amorphous silicon (DSi and ASi), providing an essential nutrient for downstream diatoms. Evidence suggests that glacially exported DSi is isotopically light compared to DSi in non-glaciated rivers. However, the isotopic fractionation mechanisms are not well constrained, indicating an important gap in our understanding of processes in the global Si cycle. We use rock crushing experiments to mimic subglacial physical erosion, to provide insight into subglacial isotope fractionation. Isotopically light DSi (δ^{30} Si_{DSi}) released following initial dissolution of freshly ground mineral surfaces (down to -2.12 ± 0.02 ‰) suggests mechanochemical reactions induce isotopic

fractionation, explaining the low δ^{30} Si_{DSi} composition of subglacial runoff. ASi with a consistent isotopic composition is present in all mechanically weathered samples, but concentrations are elevated in samples that have undergone more intense physical grinding. These experiments illustrate the critical role of physical processes in driving isotopic fractionation and biogeochemical weathering in subglacial environments. Understanding perturbations in high latitude Si cycling under climatic change will likely depend on the response of mechanochemical weathering to increased glacial melt.

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Introduction

Glaciers and ice sheets are dynamic sources of nutrients and reactive particulate material to downstream ecosystems (*e.g.*, Wadham *et al.*, 2010; Hawkings *et al.*, 2015; Sharp and Tranter, 2017). There is evidence that silicate mineral weathering is enhanced beneath large ice sheets (Wadham *et al.*, 2010; Michaud *et al.*, 2016), which may contribute significant fluxes of dissolved silicon and dissolvable amorphous silica (DSi and ASi respectively) downstream, stimulating productivity of siliceous organisms (Hendry *et al.*, 2019).

The stable silicon isotopic composition (denoted by δ^{30} Si) of glacial meltwaters can aid mechanistic understanding of subglacial weathering processes (Opfergelt *et al.*, 2013; Hawkings *et al.*, 2018; Hatton *et al.*, 2019a). Previous work has hypothesised that physical weathering in the subglacial environment results in isotopically light DSi in glacial meltwaters when compared to non-glacial riverine waters (Hatton *et al.*, 2019b). This is likely due to the creation of highly reactive mineral surfaces combined with chemical precipitation-dissolution reactions, which result in the formation and preferential dissolution of isotopically depleted amorphous weathering crusts (Opfergelt *et al.*, 2013; Hatton *et al.*, 2019b). The high levels of physical erosion and sediment comminution in subglacial environments, combined with chemical weathering act to enhance the export of DSi from subglacial environments. However, a better understanding of subglacial silicate dissolution and associated Si isotopic fractionation is required to constrain the impacts of changing glacial environments on wider associated elemental cycles (*e.g.*, nutrient liberation from silicate minerals and long term carbon drawdown from silicate weathering) and enable the inclusion of glacially exported Si in global biogeochemical models.

A large proportion of the glacial Si flux is likely exported as ASi. Field observations from Leverett Glacier, Greenland reveal up to 95 % of Si exported is ASi, which is soluble in downstream marine environments (Hawkings *et al.*, 2017). The potential ASi formation mechanisms to explain elevated glacial ASi concentrations include dissolution-reprecipitation weathering where ASi forms *via* supersaturation at the grain boundary (Hellmann *et al.*, 2012), and chemically leached particle surface layers resulting in an amorphous crust of less soluble ions such as Si (Casey *et al.*, 1993). Additionally, silicate dissolution and ASi formation have been linked to physical processes, with ASi hypothesised to form as a disturbed surface layer (Blackburn *et al.*, 2019; Hatton *et al.*,

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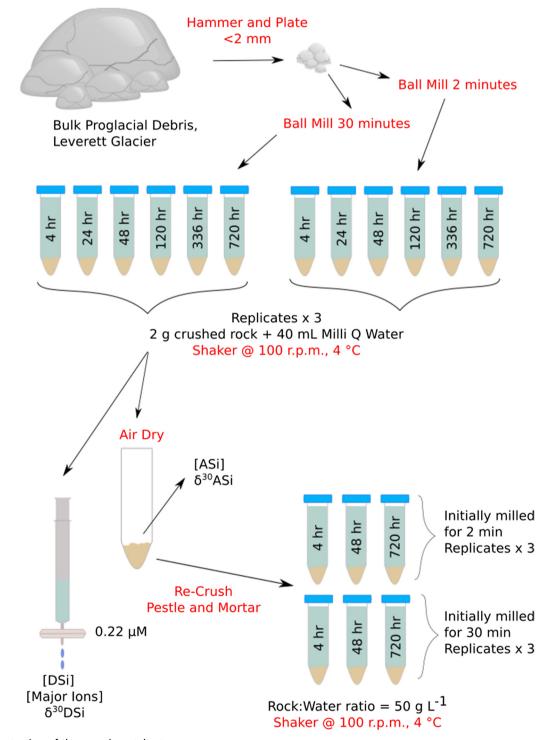
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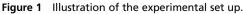
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2019b). This combination of physical erosion and chemical weathering (*i.e.* mechanochemical) could be key to understanding subglacial processes, considering high erosion rates and large surface areas of sediments in subglacial environments.

We tested the hypotheses that high physical erosion rates in subglacial environments result in (i) isotopically light DSi *via* the production of highly reactive fine grained glacial flour (Opfergelt *et al.*, 2013; Hatton *et al.*, 2019b), and (ii) the formation of ASi. Dissolution experiments (Fig. 1) mimicked mechanochemical processes in the subglacial system to ascertain the role of physical weathering on Si concentrations and δ^{30} Si composition (see Supplementary Information for full methodology). Pre-weathered unsorted glacial till (dominantly plagioclase and quartz; Fig. S-1) from Leverett Glacier proglacial plain (LG; Fig. S-2) was mechanically milled for either 2 (T2) or 30 (T30) minutes in an agate mill (note that ASi concentrations produced when milling in agate or steel mills were within analytical error, showing no significant contamination source from the agate mill, see Supplementary Information) and reacted for up to 720 hours with ultra-pure water (18.2 M Ω cm, Millipore®). The milled and reacted powders were then re-dried, re-crushed and reacted again to mimic ongoing physical erosion within a subglacial







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environment (Fig. 1). We chose to use field collected samples for these experiments to better mimic real world conditions and compare to existing field data.

Results and Discussion

Dissolution of freshly exposed mineral surfaces drives isotopically light DSi. Our experiments highlight the likely importance of physical erosion processes in subglacial environments. Rapid dissolution of Si after initial milling and after re-crushing led to δ^{30} Si_{DSi} values (down to -2.12 ‰) more depleted than values recorded in subglacial meltwater sourced DSi (+1.01 to -0.58 %); Hatton *et al.*, 2019b). The lowest δ^{30} Si_{DSi} composition for T2 and T30 was measured after 4 hours, with $\delta^{30}Si_{DSi}$ increasing over time (Fig. 2, Table S-1). The preferential release of lighter Si isotopes during dissolution relates to the distribution of ²⁸Si and ²⁹Si on surface layers. Our experiments agree with previous experiments that show physical grinding leads to the preferential release of ²⁸Si during initial dissolution of fresh surface layers, which suggests a higher abundance of ²⁸Si on the surface of freshly ground minerals in the destabilised outer layers of the crystal structure (Ziegler et al., 2005). It's likely that the high

surface areas created by physical grinding led to rapid initial dissolution of Si, with the largest isotopic fractionation. As the experiment progressed, the $\delta^{30}Si_{DSi}$ composition increased toward $\delta^{30}Si_{Bulk}$ values (Fig. 2) as proportionally more ²⁹Si was liberated from internal crystalline structures.

After the reacted material was re-crushed, the $\delta^{30}Si_{DSi}$ composition decreased again (down to -1.29 %; Fig. 2, Table S-2). The decrease in $\delta^{30}Si_{DSi}$ composition after re-crushing, suggests that the regeneration of reactive mineral surface layers by physical action promotes further dissolution of isotopically light Si. This process presents a viable mechanism to explain isotopically light DSi in glacial meltwaters, due to the continuous comminution of bedrock in the subglacial system.

Our findings of initial dissolution resulting in low $\delta^{30}Si_{DSi}$ composition are consistent with results of leaching experiments on basaltic lavas (Ziegler *et al.*, 2005) and diatom opal (Demarest *et al.*, 2009), suggesting this process is independent of sediment lithology. While our experiments do not isolate the exact mechanism driving the apparent fractionation during initial dissolution, they do suggest that continuous comminution of subglacial sediments results in exposure of fresh, large surface areas. This reactive surface layer promotes the dissolution of Si and

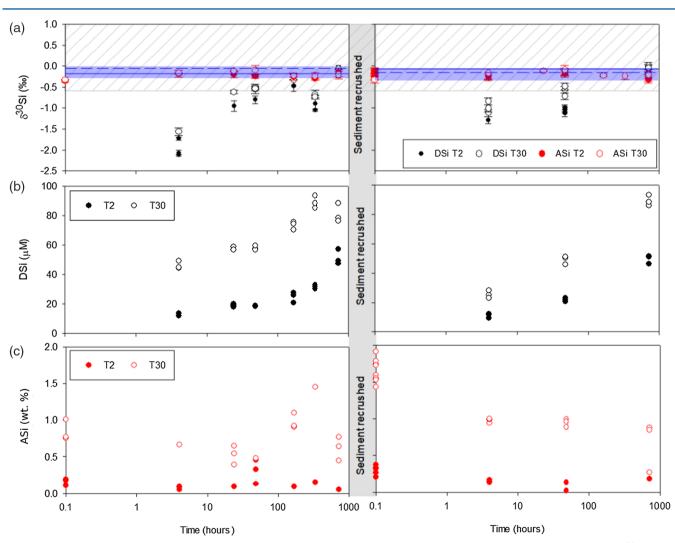


Figure 2 Geochemical results of primary and crushing experiments over time. DSi = black, ASi = red, closed = T2, open = T30. (a) δ^{30} Si_{DSi} and δ^{30} Si_{ASi} composition, error bars represent average external error (0.08 ‰, 2 s.d.). Blue horizontal lines mark δ^{30} Si composition of bulk rock (T2 = solid, T30 = dashed), with 2 s.d. external error shaded blue. (b) DSi concentrations. (c) ASi concentrations. Initial and secondary milled data separated by vertical grey area. Glacial river δ^{30} Si_{DSi} range from -0.58 to +1.01 ‰ (grey hashed region) and glacial δ^{30} Si_{ASi} ranges from -0.86 to -0.05 ‰ (Hatton *et al.*, 2019b).

drives the light δ^{30} Si_{DSi} composition in glacial meltwaters (Opfergelt *et al.*, 2013; Hatton *et al.*, 2019b).

The degree of isotopic fractionation does not appear to scale with DSi concentration and the available surface area. T2 experiments had lighter $\delta^{30}Si_{DSi}$ composition than T30 for all timepoints (Fig. 2), despite lower DSi concentrations (Fig. 2) and lower specific surface area deduced from mean grain size of material (Fig. S-3; Telling et al., 2015). There are potential explanations for this, considering i) isotopic heterogeneity within the starting material, ii) natural pre-weathering of rock material, and/or iii) ASi formation and dissolution. The rocks used in this experiment from the proglacial plain, are naturally heterogeneous, and were pre-weathered within the sub- and proglacial environment. We see evidence of amorphous SiO₂ nanoparticles in all samples via HR-TEM imaging (see Fig. 4), highlighting a degree of environmental pre-weathering prior to sample collection. This pre-weathering of material could have resulted in surface layers with a lower δ^{30} Si composition compared to the bulk rock material due to the fractionation induced by weathering processes (Frings et al., 2016). When the rocks were milled for a short time (T2), the fresh mineral surfaces were comparatively enriched with Si from these pre-weathered surfaces (e.g., isotopically light amorphous nanoparticles). Whereas, longer milling in T30 exposed more of the non-weathered crystalline structure from where proportionally more DSi was derived. This could explain why T30 DSi was marginally closer to the bulk rock value $(-0.13 \pm 0.16 \%)$. Alternatively, the higher ASi concentrations in T30 experiments may have impacted the overall $\delta^{30}Si_{DSi}$ composition. Previous experiments have shown large isotopic fractionations (up to -7.5 %) associated with quartz cement dissolution and precipitation (Basile-Doelsch et al., 2005). If there was proportionally greater ASi dissolution in T30 experiments, when compared to T2 experiments, then this could have resulted in a smaller overall fractionation in T30 and a less depleted $\delta^{30} Si_{DSi}$ composition.

Our experiments do not allow for a detailed analysis of the difference in $\delta^{30} Si_{DSi}$ composition between T2 and T30 resulting from dissolution, particularly with the potential impacts of the environmental pre-weathering. However, the overall differences are small compared to the large fractionation observed after initial dissolution. Therefore, we hypothesise that continuous subglacial physical erosion of bedrock could lead to isotopically low $\delta^{30}Si_{DSi}$ after wetting sediments with dilute waters. This process would likely explain the observed low meltwater $\delta^{30}Si_{DSi}$ composition (Hatton *et al.*, 2019b).

Mechanochemical reactions may promote ASi formation in subglacial systems. A more robust understanding of the formation process of subglacial ASi is important considering the large flux term of glacial ASi to downstream environments (Hawkings et al., 2017). We use these experiments to deduce the potential role of physical erosion in ASi formation. ASi concentrations were consistently higher in T30 compared to T2 (Fig. 3, Tables S-1, S-2) after both the initial milling $(T30 \sim 0.8 \% \text{ d.w.}, T2 \sim 0.2 \% \text{ d.w.})$ and then re-crushing (T30 ~ 1.2 % d.w., T2 ~ 0.3 % d.w.), indicating that more intense physical erosion and generation of larger particle surface areas resulted in higher observed ASi concentrations. The increase in ASi from the end of the initial dissolution to when the material was re-crushed also indicates that the secondary crushing regenerates fresh amorphous mineral surfaces. It is likely that the milling process results in greater ASi formation, which is more soluble as a result of a greater surface area from longer milling times. Elevated ASi concentrations from crushing are consistent with field observations of ASi-rich precipitates produced by subglacial physical and chemical weathering processes during the last glaciation (Blackburn et al., 2019), and ASi formation by

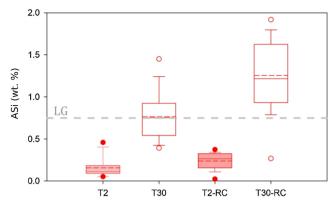


Figure 3 ASi concentrations, grouped as T2, T30 (initial milling and dissolution), and T2-RC, T30-RC (secondary crushing and dissolution), with median (solid) and mean (dashed) shown. Grey dashed line represents discharge weighted mean ASi concentration from proglacial river of Leverett Glacier (LG) in 2015 (Hatton *et al.*, 2019a).

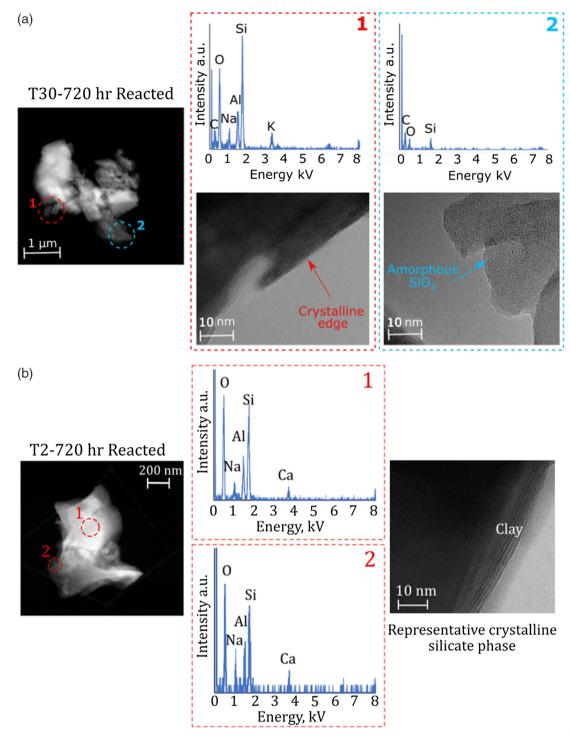
comminution and associated breakdown of crystalline structures (Yund *et al.*, 1990).

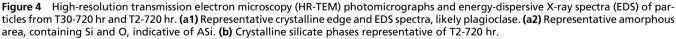
A confounding factor is that HR-TEM photomicrographs indicate the presence of amorphous SiO₂ nanoparticle aggregates in all samples (Fig. 4). There was also no statistical difference in overall crystallinity between starting material and milled material when completing pair distribution function (PDF) analysis of the X-ray scattering, though observable peak differences were present (Fig. S-4). These small concentrations of chemically sourced ASi observable under HR-TEM, likely result from environmental preweathering. Despite this, the low ASi concentrations of unmilled control experiments (avg. 0.11 % d.w.; Table S-6) combined with the elevated ASi concentrations for all T30 experiments (avg. 1.03 % d.w.), provide strong evidence for the importance of intense physical erosion in amorphisation and the mobilisation of pre-existing reactive Si, mimicking the subglacial environment.

The δ^{30} Si_{ASi} composition (Fig. 2) was not significantly different over the incubation timescale (ANOVA, p value 0.06), between T2 and T30 (ANOVA, p value 0.83), and after recrushing (ANOVA, p value 0.87), with an overall average δ^{30} Si_{ASi} of -0.22 ± 0.15 ‰ (2 s.d.). It is likely that this relatively consistent δ^{30} Si_{ASi} composition is linked to the large ASi reservoir compared to DSi. Our experimental values are similar in composition to field measurements over a summer melt season at LG (-0.32 to -0.11 ‰; Hatton *et al.*, 2019a), demonstrating the likely similarities between the subglacial processes forming ASi in the field and in our experiments.

Implications for Subglacial Silicon Cycling

Our findings highlight the importance of mechanochemical processes beneath glaciers for silicon cycling despite near freezing water temperatures. Our study improves understanding of the mechanistic drivers of subglacial Si cycling, which will help inform wider biogeochemical models. Our experiments highlight the potential of glacial physical weathering in creating high concentrations of labile ASi and a distinct isotopic signature for DSi. Physical erosion appears essential in creating fresh reactive mineral surfaces that lead to the dissolution of isotopically light DSi in subglacial environments. It is therefore likely that actively eroding glaciers with high suspended sediment concentrations and an active subglacial hydrological system will export





meltwaters with isotopically light DSi compared to non-glacial rivers. The variation in $\delta^{30} {\rm Si}_{\rm DSi}$ composition and ASi concentrations between glacierised catchments could be explained by differences in erosional processes, such as heterogeneity within and between glacial ice flow rates, subglacial hydrological conditions, starting bedrock composition, and resulting mobilised sediment surface areas. Further work considering mechanistic processes using pristine starting minerals could be beneficial. Such work, combined with our findings would be key to informing a developed conceptual model of glacial biogeochemical

weathering processes to consider the sensitivity of glacier and ice sheet melt to climatic warming, and the potential role of these systems in global elemental cycling.

Author Contributions

JEH and KRH conceived the study. JEH, RB, VR, LGB, HCN and TW completed laboratory analysis. All authors were involved in writing the manuscript, data interpretation and discussion.

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Additional Information

Supplementary Information accompanies this letter at https:// www.geochemicalperspectivesletters.org/article2126.



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