

WP2, D2.1 D7 Rate of release of solutes and gases from reactivated crushed glacial flour

Project number:	101072761
Project name:	Center for Glacial Biome Doctoral Network
Project acronym:	ICEBIO
Call:	HORIZON-MSCA-2021-DN-01
Topic:	HORIZON-MSCA-2021-DN-01-01
Type of action:	HORIZON-TMA-MSCA-DN
Service:	REA/A/01
Project start date:	1 October 2022
Project duration:	48 months
Deliverable title:	Rate of release of solutes and gases from reactivated crushed glacial flour
Deliverable number:	D2.1
Type:	Document, report
Due date (month)	28
Lead beneficiary:	AU
Dissemination level:	PU – Public
Work package number:	WP2
Lead author:	Klara Köhler
Author(s):	Klara Köhler
Reviewed by:	Martyn Tranter, Beatriz Gill Olivas, Alexandre Anesio
Approved by:	Martyn Tranter, Beatriz Gill Olivas, Alexandre Anesio



**Funded by
the European Union**



DISCLAIMER

The ICEBIO project is funded by the European Union under the HORIZON-MSCA-2021-DN-01 program, project number 101072761. Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held

Introduction

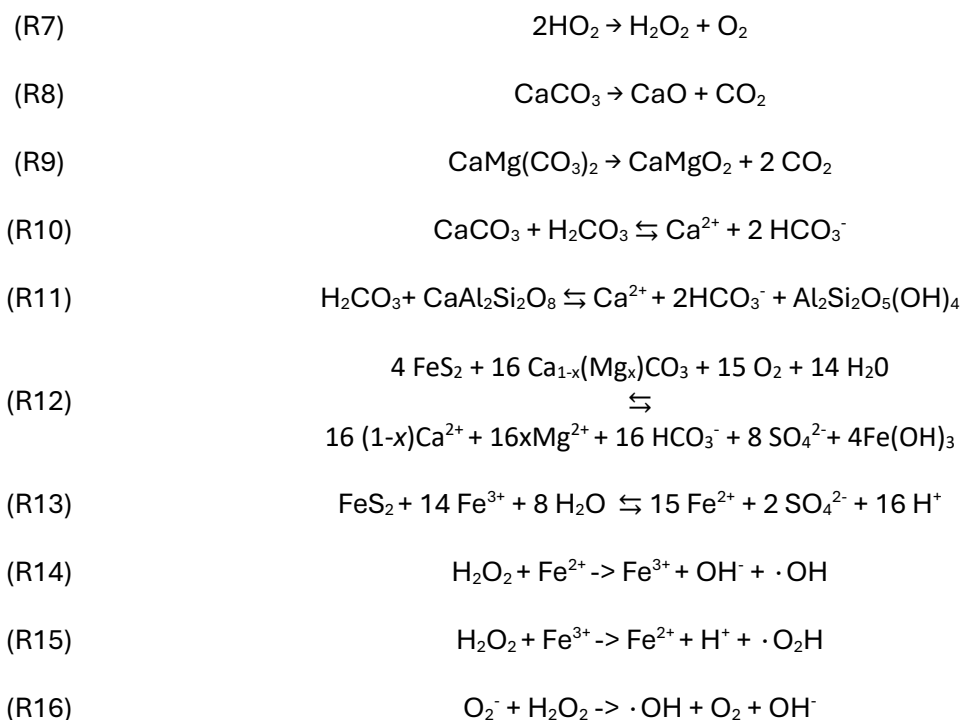
Subglacial comminution, the mechanical breakdown of bedrock and sediments beneath glaciers, plays a crucial role in shaping the subglacial environment. This process generates fine-grained sediments with fresh, unweathered mineral surfaces and high surface-area-to-volume ratios, making them highly reactive (Anderson, 2005). The grinding and abrasion of subglacial bedrock by glaciers are essential for biogeochemical cycling of nutrients such as silicon (Si), nitrogen (N), phosphorus (P), and iron (Fe). Studies have well established the link between physical and chemical weathering and its impact on subglacial meltwater chemistry (e.g. Hodson et al., 2004; Anderson, 2005; Raiswell et al., 2006; Tranter, 2006), as well as the influence of microbial communities on these reactions (e.g. Tranter et al., 2005; Hodson et al., 2008; Skidmore et al., 2010). However, direct studies on the release of bioavailable nutrients due to bedrock comminution are sparse. To date, studies looking at the effect of comminution on subglacial environments have mostly focused on the release of gases and microbial energy sources (Telling et al., 2015; Macdonald et al., 2018; Gill Olivas et al., 2021, 2023; Gill-Olivas et al., 2024).

The crushing of silicate minerals within the subglacial environment can generate hydrogen (H_2) and hydrogen peroxide (H_2O_2). H_2 can be produced when Si and O-Si radicals, formed during the rupture of Si-O bonds, react with meltwater (R1-R3; Kita et al., 1982; Telling et al., 2015). Si-O bonds broken by heterolytic cleavage generate H^+ when they react with water (R4; Stillings et al., 2021). H_2O_2 is formed when silicate radicals react with oxygen under aerobic conditions (R5-7; Gill Olivas et al., 2021). Transient high temperatures ($120^\circ C$) can shift the balance towards more H_2O_2 generation and less H_2 production (Stone et al., 2023).

CO_2 can be produced in subglacial environments through microbial respiration and oxidation of organic matter (Sharp et al., 1999), the release from fluid inclusions (Diamond, 2001) and the comminution of inorganic C-containing rocks like calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) (R8-9; Macdonald et al., 2018). The CO_2 released from rock crushing dissolves in water, forming H_2CO_3 , which drives further chemical weathering reactions, dissolving both carbonate (R10) and silicate (R11; Tranter et al., 2002; Macdonald et al., 2018).

During pyrite oxidation in subglacial environments, iron(oxy)hydroxides ($Fe(OH)_3$) are formed while consuming oxygen (R12; Tranter, 2003). The Fe^{3+} produced can further oxidize pyrite in anoxic environments (R13; Tranter, 2003). The release of Fe^{2+} allows the Haber-Weiss reaction to occur, generating O_2 , $\cdot OH$, and OH^- from H_2O_2 (R14-16; Haber and Weiss, 1932; Gil-Lozano et al., 2017; Gill Olivas et al., 2023).





Outline for experimental set up to further study the release from reactivated crushed glacial flour

In a first ICEBIO experiment, crushed sediment was mixed with ultrapure water directly after crushing and the concentration of Si, P, Fe and N into solution was measured. The results already show a difference of released nutrients when comparing crushed and non-crushed sediments. The release of Si, P and Fe from the sediment into solution is significantly higher for the crushed sediments compared to non-crushed sediments. For the N-species, the concentration of N in solution in form of NO_2^- is higher for crushed sediments, while the release of NO_3^- is higher for non-crushed sediments. For the concentration of NH_4^+ in solution there is no significant difference between crushed versus non-crushed sediments.

Further to this initial experiment, we outline here a crushing set up to follow up on these first findings (Figure 1). The aim is to further explore how the comminution of glacial sediment samples such as glacial flour and basal debris directly impact the release of bioavailable nutrients from reactivated crushed glacial flour. In order to do so, glacial samples like fine glacial sediment and basal debris collected at the margin or from the subglacial environment of a glacier should be used. It is important to determine the mineralogy of the rocks and sediment in a set-up with natural samples, as, for example, impurities such as carbonates in silicate rocks could affect the reaction products of abrasion processes (Gill-Olivas et al., 2024).

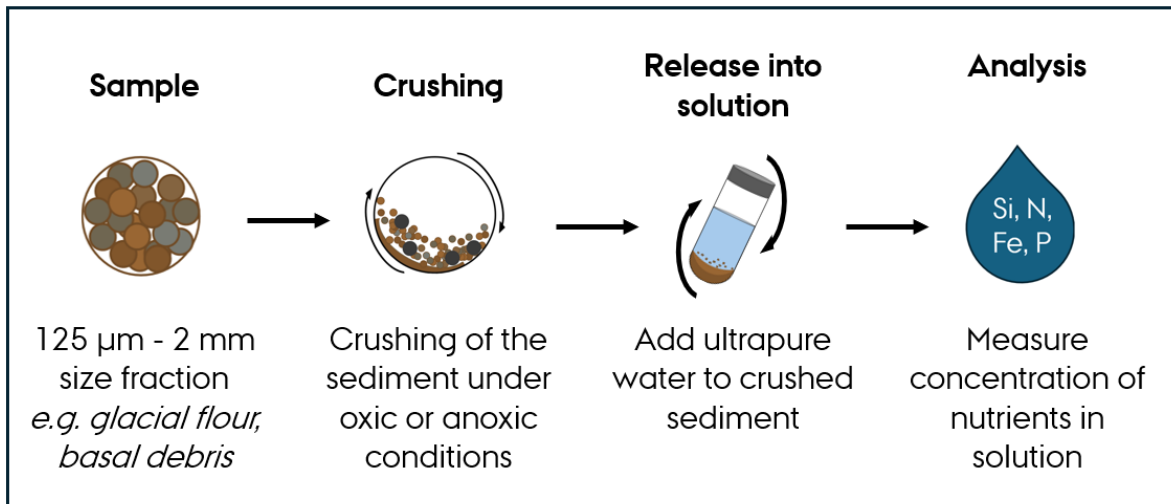


Figure 1: Outline for a crushing experiment to study the release of nutrients (Si, N, Fe, P) into solution.

In the suggested setup, rock samples are broken into smaller pieces using a sledgehammer and a steel plate prior to milling. The dried debris and sediment samples are sieved to obtain the 2mm- 125 μ m size fraction and crushed using a gas-tight agate ball mill. The crushing can be conducted under oxic and under anoxic (under a N₂ headspace) to simulate different REDOX conditions found in subglacial environments. Previous crushing experiments have been conducted using dry sediments (e.g. Telling et al., 2015; Gill Olivas et al., 2023). However, to mimic the subglacial environment and to explore what immediate rock-water reactions take place during crushing, the same experimental set up should be conducted once with dry and once with wet sediments. Aliquots of the crushed sediment samples are transferred into centrifuge tubes and ultrapure water is added. The water is hereafter measured for the concentration of Si, N, Fe and P to study to what extent the nutrients are released into solution from the sediment samples directly after crushing.

References

- Anderson, S. P. (2005). Glaciers show direct linkage between erosion rate and chemical weathering fluxes. *Geomorphology* 67, 147–157. doi: 10.1016/j.geomorph.2004.07.010
- Diamond, L. W. (2001). Review of the systematics of CO₂–H₂O fluid inclusions. *Lithos* 55, 69–99. doi: 10.1016/S0024-4937(00)00039-6
- Gill Olivas, B., Telling, J., Skidmore, M., and Tranter, M. (2023). Abrasion of sedimentary rocks as a source of hydrogen peroxide and nutrients to subglacial ecosystems. doi: 10.5194/egusphere-2022-908
- Gill Olivas, B., Telling, J., Tranter, M., Skidmore, M., Christner, B., O’Doherty, S., et al. (2021). Subglacial erosion has the potential to sustain microbial processes in Subglacial Lake Whillans, Antarctica. *Commun Earth Environ* 2, 134. doi: 10.1038/s43247-021-00202-x
- Gill-Olivas, B., Telling, J., and Tranter, M. (2024). Geochemical reactions initiated by subglacial abrasion of natural quartz and alkali feldspar. *Front. Earth Sci.* 12. doi: 10.3389/feart.2024.1371128
- Gil-Lozano, C., Davila, A. F., Losa-Adams, E., Fairén, A. G., and Gago-Duport, L. (2017). Quantifying Fenton reaction pathways driven by self-generated H₂O₂ on pyrite surfaces. *Scientific Reports* 7. doi: 10.1038/srep43703
- Haber, F., and Weiss, J. (1932). Über die Katalyse des Hydroperoxydes. *Naturwissenschaften* 20, 948–950. doi: 10.1007/BF01504715
- Hodson, A., Anesio, A. M., Tranter, M., Fountain, A. G., Osborn, M., Priscu, J. C., et al. (2008). Glacial Ecosystems. *Ecological monographs* 78, 41–67.
- Hodson, A., Mumford, P., and Lister, D. (2004). Suspended sediment and phosphorus in proglacial rivers: bioavailability and potential impacts upon the P status of ice-marginal receiving waters. *Hydrol. Process.* 18, 2409–2422. doi: 10.1002/hyp.1471
- Kita, I., Matsuo, S., and Wakita, H. (1982). H₂ generation by reaction between H₂O and crushed rock: An experimental study on H₂ degassing from the active fault zone. *Journal of Geophysical Research: Solid Earth* 87, 10789–10795. doi: 10.1029/JB087iB13p10789
- Macdonald, M. L., Wadham, J. L., Telling, J., and Skidmore, M. L. (2018). Glacial Erosion Liberates Lithologic Energy Sources for Microbes and Acidity for Chemical Weathering Beneath Glaciers and Ice Sheets. *Front. Earth Sci.* 6, 212. doi: 10.3389/feart.2018.00212
- Raiswell, R., Tranter, M., Benning, L. G., Siegert, M., De’ath, R., Huybrechts, P., et al. (2006). Contributions from glacially derived sediment to the global iron (oxyhydr)oxide cycle: Implications for iron delivery to the oceans. *Geochimica et Cosmochimica Acta* 70, 2765–2780. doi: 10.1016/j.gca.2005.12.027
- Sharp, M., Parkes, J., Cragg, B., Fairchild, I. J., Lamb, H., and Tranter, M. (1999). Widespread bacterial populations at glacier beds and their relationship to rock weathering and carbon cycling. *Geology* 27, 107–110. doi: 10.1130/0091-7613(1999)027<0107:WBPAGB>2.3.CO;2
- Skidmore, M., Tranter, M., Tulaczyk, S., and Lanoil, B. (2010). Hydrochemistry of ice stream beds—evaporitic or microbial effects? *Hydrological Processes* 24, 517–523. doi: 10.1002/hyp.7580
- Stillings, M., Lunn, R. J., Pytharouli, S., Shipton, Z. K., Kinali, M., Lord, R., et al. (2021). Microseismic Events Cause Significant pH Drops in Groundwater. *Geophysical Research Letters* 48, e2020GL089885. doi: 10.1029/2020GL089885
- Stone, J., Edgar, J. O., Rutherford, J., Gill-Olivas, B., Tranter, M., Gould, J. A., et al. (2023). Flash heating boosts the potential for mechanochemical energy sources for subglacial ecosystems. *Frontiers in Geochemistry*. doi:10.3389/fgeoc.2023.1180893
- Telling, J., Boyd, E. S., Bone, N., Jones, E. L., Tranter, M., MacFarlane, J. W., et al. (2015). Rock comminution as a source of hydrogen for subglacial ecosystems. *Nature Geosci* 8, 851–855. doi: 10.1038/ngeo2533

- Tranter, M. (2003). "5.07 - Geochemical Weathering in Glacial and Proglacial Environments," in *Treatise on Geochemistry*, eds. H. D. Holland and K. K. Turekian (Oxford: Pergamon), 189–205. doi: 10.1016/B0-08-043751-6/05078-7
- Tranter, M. (2006). "Glacial chemical weathering, runoff composition and solute fluxes," in *Glacier science and environmental change*, ed. Peter G. Knight (Blackwell Science Ltd, a Blackwell Publishing company), 71–75.
- Tranter, M., Sharp, M. J., Lamb, H. R., Brown, G. H., Hubbard, B. P., and Willis, I. C. (2002). Geochemical weathering at the bed of Haut Glacier d’Arolla, Switzerland—a new model. *Hydrological Processes* 16, 959–993. doi: 10.1002/hyp.309
- Tranter, M., Skidmore, M., and Wadham, J. (2005). Hydrological controls on microbial communities in subglacial environments. *Hydrological Processes* 19, 995–998. doi: 10.1002/hyp.5854