

James T. Davidson*
Jon Telling
&
John O. Edgar

*J.davidson5@newcastle.ac.uk

*School of Natural and Environmental Sciences,
 Newcastle University,
 Newcastle upon Tyne,
 NE1 7RU, UK*

Key Literature:

Baga, A.N., Johnson G.R.A., Nazhat, N.B., and Saadalla-Nazhat, R.A., (1988), "A simple spectrophotometric determination of hydrogen peroxide at low concentrations in aqueous solutions," *Anal. Chim. Acta*, Vol. 204, pp. 349–353.

Bak, E. N., et al. (2017). "Production of reactive oxygen species from abraded silicates. Implications for the reactivity of the Martian soil." *Earth and Planetary Science Letters*, Vol. 473, pp. 113-121.

Christner, B. C., et al. (2014). "A microbial ecosystem beneath the West Antarctic ice sheet, *Nature*, Vol. 512 (7522), pp. 310-315.

Kita, I., S. Matsuo and H. Wakita (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* Vol. 87 (10), pp.789-795.

Macdonald, M. L., et al. (2018). "Glacial Erosion Liberates Lithologic Energy Sources for Microbes and Acidity for Chemical Weathering Beneath Glaciers and Ice Sheets." *Frontiers In Earth Science*, Vol. 6 (12), pp.1-15.

Parkes, R. J., et al. (2019). "Rock-crushing derived hydrogen directly supports a methanogenic community: significance for the deep biosphere." *Environmental Microbiology Reports*, Vol. 11(2), pp.165-172.

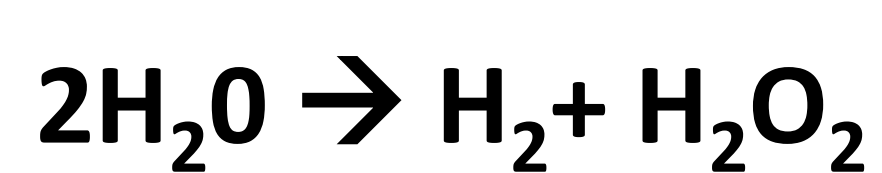
Telling, J., et al. (2015). "Rock comminution as a source of hydrogen for subglacial ecosystems." *Nature Geoscience*, Vol. 8 (12), pp. 851-855.

The Daily Grind:

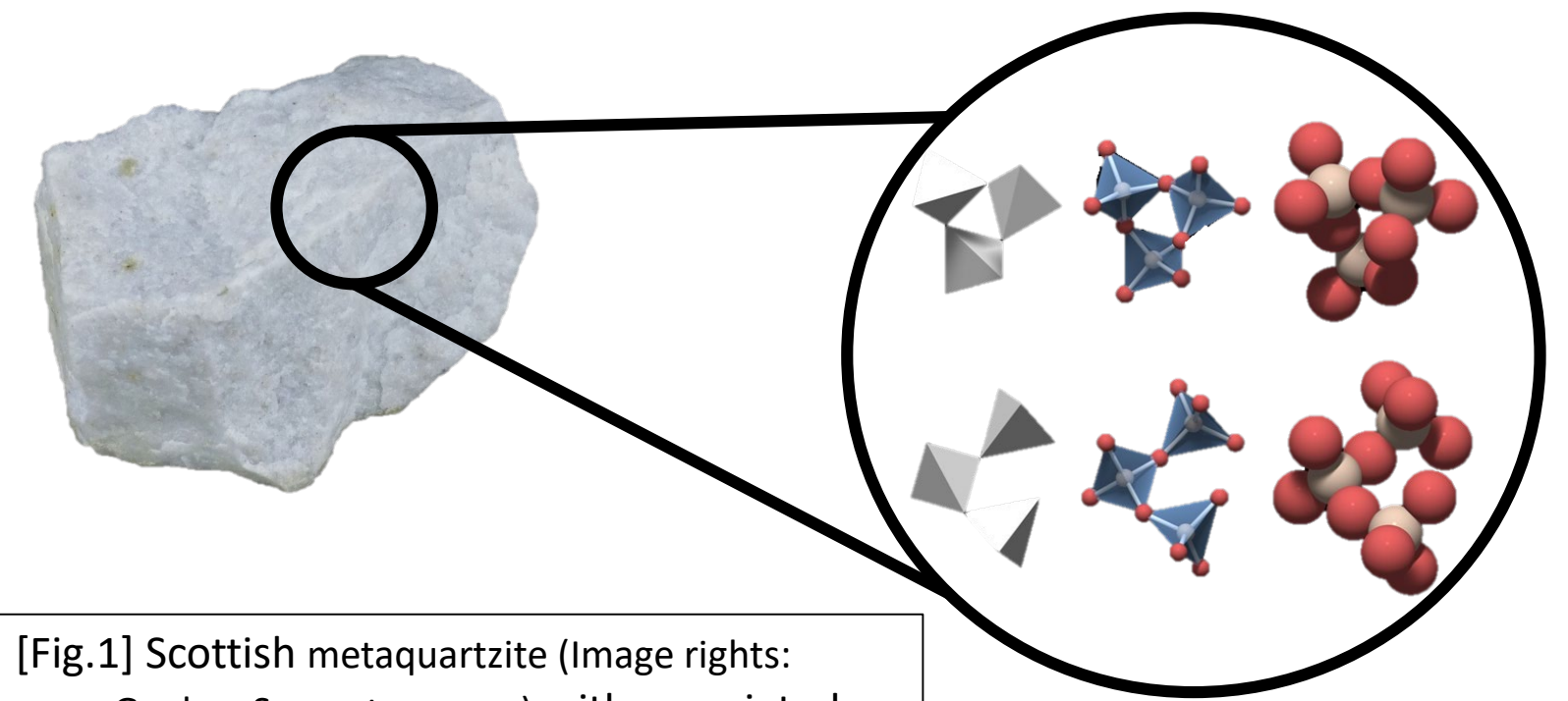
Glaciers and ice sheets as pressurized mechanochemical reactors

Summary

When a flint is struck against a flint, a spark is formed. This is produced by broken 'dangling' bonds (free radicals) on the fractured flint surfaces reacting with the atmosphere, releasing enough energy to produce a spark. Under glaciers and ice sheets, similar 'mechanochemical' reactions take place when rocks embedded in the glacier beds grind over bedrock and sediment, reacting to split liquid water to produce hydrogen gas and oxidants (Kita et al. 1982). These products can fuel the growth and activity of microbes, including those that produce methane gas – an important global warming gas (Macdonald et al. 2018). This project focuses on the relatively little studied production of the strong oxidant hydrogen peroxide (H₂O₂) during mechanochemical reactions, as a proxy for crushing reactions that may occur under glaciers, ice sheets (Telling et al. 2015) and along geological faults (Parkes et al. 2019).



[Equation.1] The splitting of water into hydrogen gas and hydrogen peroxide.

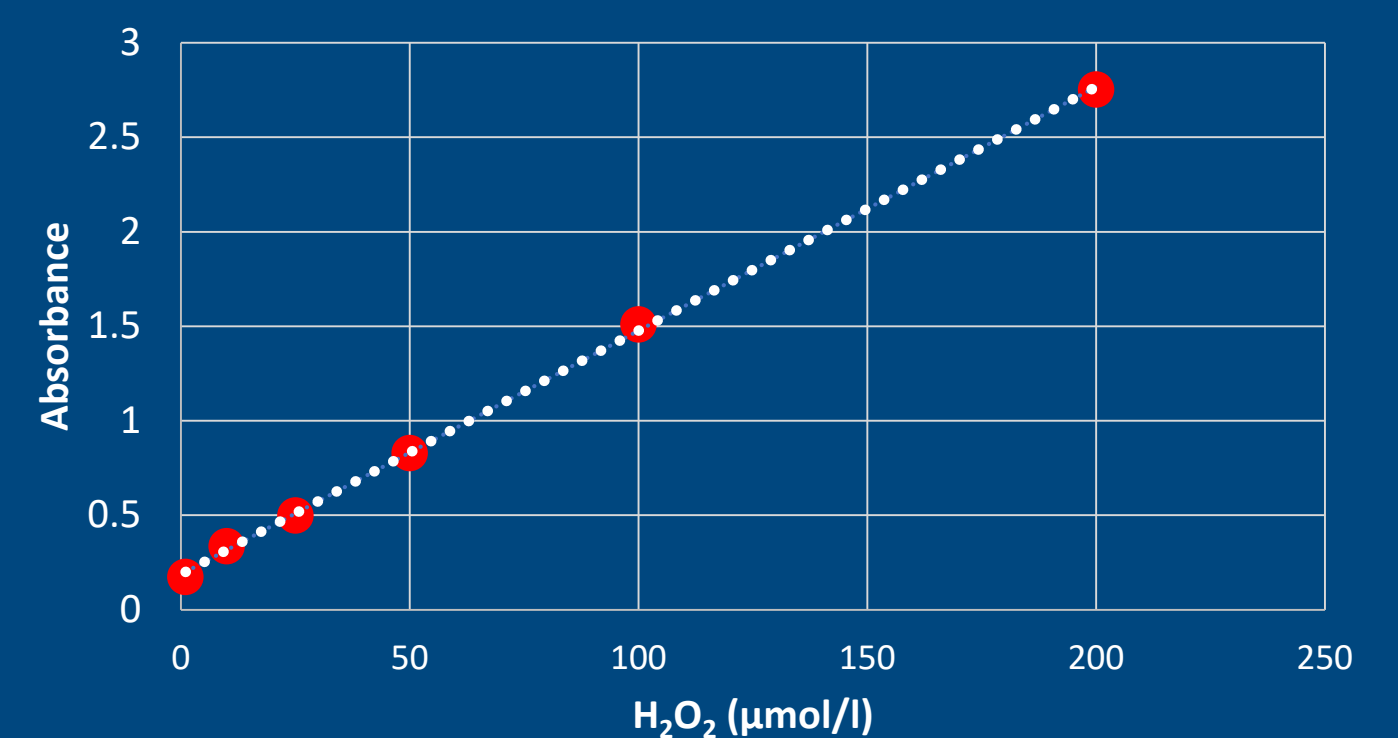


[Fig.1] Scottish metaquartzite (Image rights: www.GeologySuperstore.com) with associated silica and oxygen crystalline tetrahedral structure (Image rights: www.quartzpage.de).

Methodology

Metaquartzite samples were acquired from a commercially available source (www.GeologySuperstore.com) and subsequently crushed to produce smaller 2-3cm size chips. These chips were then loaded into a ball mill cleaned with methanol which ran for 30 seconds to produce a fine quartzite powder. Approximately 3 grams of the crushed quartzite was weighed and placed within labelled 8 ml borosilicate (for no headspace experiments) and 12 ml (for headspace experiment) vials. For samples containing no headspace, the vials were first sealed with bungs and crimped to minimise any subsequent oxidation with air. Helium was bubbled through a large 1L flask of water for 30 minutes to create anoxic conditions and remove any trace gases. This water was then injected into the vials, tilting when necessary to minimise any trapped air bubbles. For samples without headspace, an equal volume of water was added. These were then bunged and crimped.

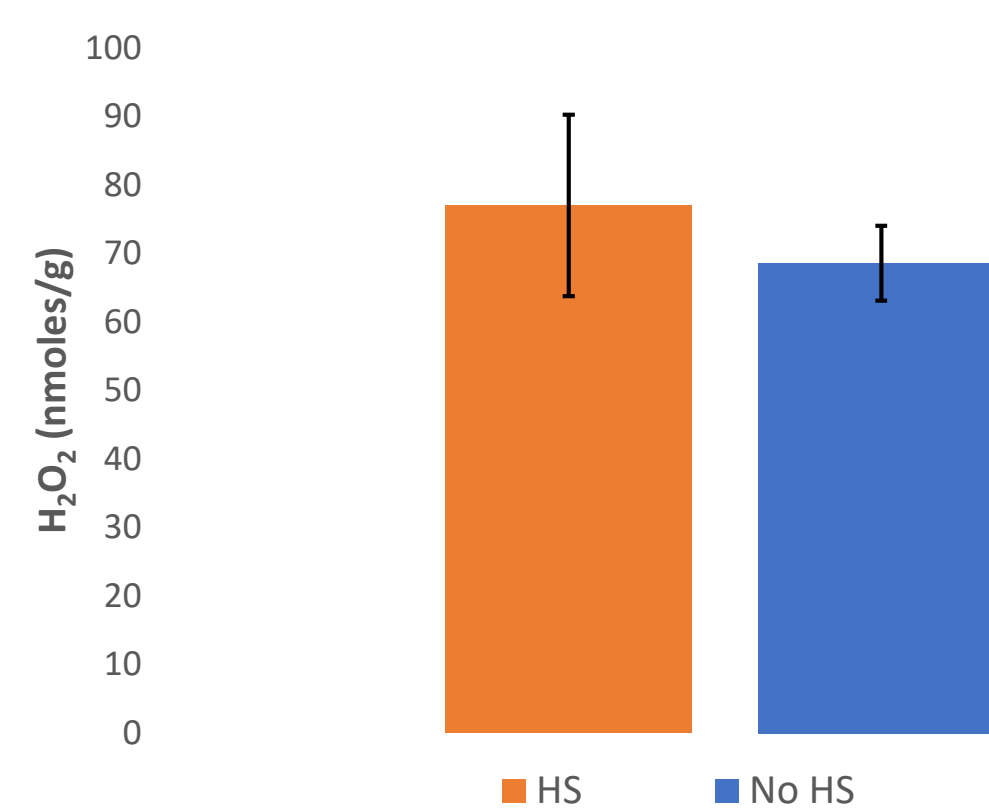
Vials were left at room temperature, and H₂O₂ production monitored in triplicate vials over 8 days following the spectrophotometric method of Baga et al. (1988). A calibration curve was produced by this assay to determine the concentration of H₂O₂ [Fig.2].



[Fig.2] Calibration curve for H₂O₂ assay .

Results

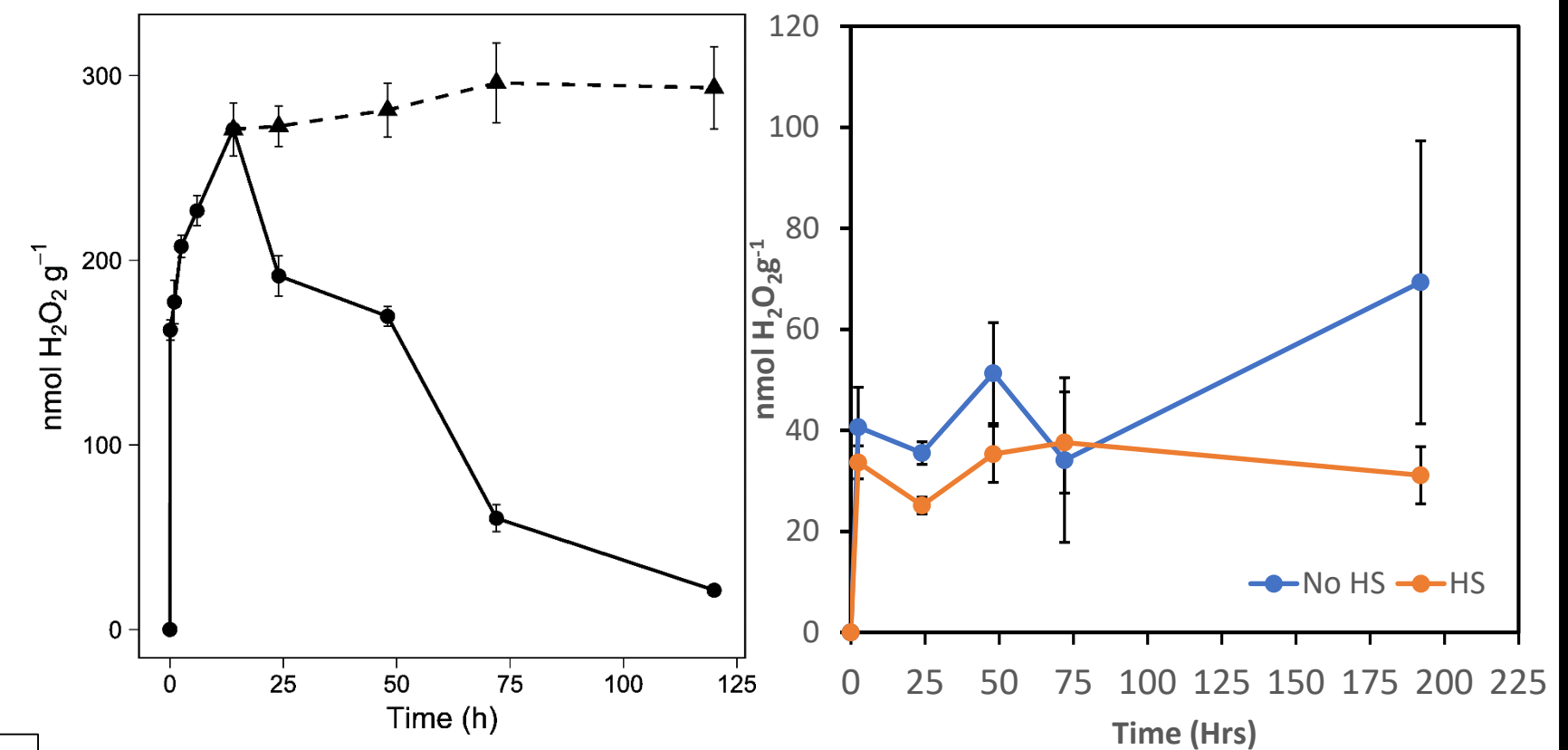
Initial results from a preliminary experiment measuring hydrogen peroxide production over a 24 hour period under oxic conditions suggested that there was no significant difference between the vials containing headspace and no headspace [Fig.3].



[Fig.3] H₂O₂ generated after 24 hours by adding crushed quartzite to H₂O under air with a headspace (HS) and no headspace (No HS). Error bars are one standard deviation.

The second experiment was carried out under oxygen free conditions and over a longer time period of 8 days. Within this, hydrogen peroxide production rose most sharply in the first hour before [Fig.5]. This follows a similar trend shown by Bak et al (2017) [Fig.4].

However, under our oxygen free conditions hydrogen peroxide concentrations were stable for at least 225 hours in contact with the crushed quartzite, in contrast to under oxic conditions where concentrations rapidly decreased (Bak et al 2017; solid line in Fig. 4).



[Fig.4] Figure taken from Bak et al. (2017) showing time dependence of H₂O₂ concentration after suspension of abraded quartz in water under oxic conditions. Dotted line shows results after solution was filtered. Solid line shows results when water remained in contact with quartz.

[Fig.5] Time series results showing H₂O₂ concentration against time after suspension of abraded metaquartzite in oxygen free water. Error bars show one standard deviation. HS is with headspace present, No HS is no headspace.

Key Findings:

- Significant concentrations of hydrogen peroxide (40 nmoles g⁻¹ quartzite) were generated within the first hour of reaction of crushed quartzite with oxygen free water, and concentrations remained stable for at least 200 hours.
- The presence of a headspace did not significantly effect the overall production of hydrogen peroxide (at 95% significance level, P= 0.123) .
- Prior experiments crushing quartzite under oxygen free conditions (Telling et al. 2015) produced hydrogen at the same order of magnitude as the H₂O₂ in the present study, consistent with a source for both from the splitting of water by mineral surface silica free radicals.

Conclusions:

In aqueous subsurface environments where mechanical crushing occurs (e.g. beneath glaciers, ice sheets (Christner et al. 2014; Telling et al. 2015, and adjacent to geological faults (Kita et al. 1982; Parkes et al. 2019), mechanochemical reactions may not only produce hydrogen gas but a similar magnitude of the strong oxidant hydrogen peroxide. This hydrogen peroxide, which appeared stable in our oxygen free experiments for over one week, may have important implications for the cycling and bioavailability of nutrients and organic carbon both under glaciers and along geological faults.

Further research is needed to assess the roles of temperature and pressure in influencing the production of hydrogen peroxide from mechanochemical reactions.