Europlanet TA Scientific Report

PROJECT LEADER

Project number: 22-EPN3-007

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TA Facility visited: Iceland

Project Title:

SEISCHEM - THE INFLUENCE OF SEISMIC EVENTS ON FLUID AND GAS CHEMISTRY
AT THE ICELANDIC PLANETARY FIELD SITE

Scientific Report Summary.

(plain text, no figures, maximum 250 words, to be included in database and published)

Measurable H_2 can be generated during active seismicity through the reaction of water with freshly created rock surfaces. Field measurements have shown that rock-water reactions during seismic events can also lead to significant changes in the pH and increase the concentration of H_2O_2 in geological fluids. Whilst prior studies have investigated locations representing felsic crust, a large proportion of the deep biosphere resides in basaltic terrains. H_2O_2 generated through rock-water reactions is greater in basaltic rocks and enhanced when temperatures exceed $^{\sim}$ 80 °C. Importantly, these elevated temperatures overlap the growth ranges of some hyperthermophilic microorganisms. The generation of H_2O_2 in these environments represents an understudied energetic window of opportunity for extant microbial life, and possibly for the origins of life on Earth. We propose to sample a seismically active hydrothermal area in Iceland where elevated temperatures are anticipated to lead to enhanced H_2O_2 generation from rock-water reactions.

SeisChem will investigate the relationship between seismicity and the products of rock - water reactions in a geologically active hydrothermal system. The central objective of SeisChem is to bridge a knowledge gap between laboratory studies and field measurements. To do this it will:

- Sample fluid and gas in time series, recording in-situ H₂O₂ and ancillary geochemical data
- Store and return samples to the laboratory for H₂ (g) and major ion (aq) analyses
- Compare and contrast field and laboratory data with local seismic activity

Full Scientific Report on the outcome of your TNA visit

Subsurface faults and fractures in the Earth's crust are often associated with high temperature fluid flow (Fig. 1a) and provide habitats for microbial ecosystems. Hydrothermal systems have also been proposed as locations of prebiotic synthesis and potentially the origins of life on Earth. Within these systems, silicate minerals are mechanically fractured producing chemically active sites via the heterolytic (Eq. 1) or homolytic (Eq. 2) breaking of covalent silica-oxygen bonds (Fig. 1b):

$$\equiv Si - O - Si \equiv \xrightarrow{fracture} \equiv Si - O^{-} + {}^{+}Si \equiv$$

$$\equiv Si - O - Si \equiv \xrightarrow{fracture} \equiv Si - O^{\bullet} + {}^{\bullet}Si \equiv$$
(1)

$$\equiv Si - O - Si \equiv \xrightarrow{\text{Future}} \equiv Si - O^{\bullet} + {}^{\bullet}Si \equiv \tag{2}$$

Where ≡ represents bonds in the surrounding silicate structure. Field measurements of pH changes following seismic events are suggested to be due to the reaction of H₂O with ⁺Si.

$$Si^+ + H_2O \rightarrow SiOH + H^+$$
 (3)

In oxygen limited environments H₂O can also react with Si producing H₂ gas, (Eq: 4; Fig. 1b):

$$2Si^{\bullet} + 2H_2O \rightarrow 2SiOH + H_2 \tag{4}$$

However, where O2 is present, Si radicals readily react to generate the surface-bound superoxide radical (SiO₂*), which can subsequently react with H₂O to generate H₂O₂ and release O₂:

$$2SiO_2^{\bullet} + 2H_2O \rightarrow 2SiOH + H_2O_2 + O_2$$
 (5)

In addition to this, at elevated temperatures SiO will react with water directly producing H₂O₂ (Stone et al., 2022; Fig. 1b):

$$2SiO^{\bullet} + 2 H_2O \xrightarrow{T \gtrsim 80 \, {}^{\circ}C} 2SiOH + H_2O_2$$
 (6)

Further to these reactions, certain microorganisms posess enzymes which facilitate the disproportionation of H₂O₂ to H₂O and O₂. Whilst H₂O₂ can be toxic to life, both H₂O₂ and O₂ can act as electron acceptors in the oxidation of H₂. Consequently, subsurface faulting and fracture systems not only provide habitats for microorganisms, through H₂ and H₂O₂ production they can supply energy for microbial maintenance and growth.

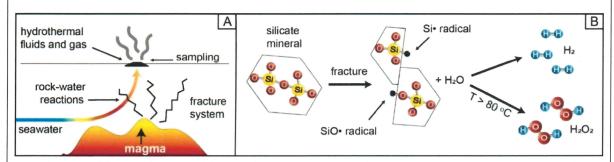


Figure 1: H_2O_2 and H_2 generation in a hydrothermal setting. A) As a magma rises it can cause fractures in overlaying rock units. Water flowing through these fracture systems will be exposed to freshy fractured rocks surfaces. B) Si and SiO radicals are generated on the surfaces of fractured silicate minerals. These reactive sites can react with water generating H₂ and H₂O₂.

If microorganisms living around subsurface fault zones could utilise theses oxidants alongside hydrogen, then this could greatly enhance the energy available for growth. A key study tracing the common genes in Archaea and Bacteria to a Last Common Universal Ancestor (LUCA) concluded that it was a hyperthermophile, autotrophic (fixed CO₂), and dependent on H₂. This has been proposed to be consistent with an origin of life around basaltic hydrothermal vents. A contradictory feature in this and all prior reconstruction of LUCA's genome was the presence of abundant genes for detoxifying H₂O₂ and O₂. As the presence of H₂O₂ and O₂ did not fit assumptions of an early Archean environment, the presence of these genes has been explained as an artefact of the later evolution of photosynthetic oxygen and subsequent multiple lateral gene transfer events. Recent research has provided an alternative explanation - that antioxidant genes were indeed part of a hyperthermophilic LUCA. We suggest these genes aided in making energetic use of the H₂O₂ and O₂ produced during the stressing and fracturing of the Earth's early crust. The most recent laboratory work suggests that high-temperature basaltic hydrothermal areas will be more H₂O₂ productive than low-temperature felsic areas, however, to our knowledge this has not been tested in the field.

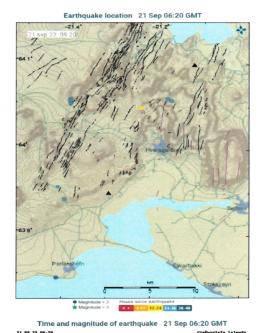
We first performed a spatial survey where we checked the chemical parameters of a number of different pools, across two site. From this information we were able to select two pools for prolonged sampling. These represent acidic (~ pH 2.5) and near neutral (~ pH 6.5) conditions. At the field site we set up a field tent to house our sensitive H₂O₂ sensor and the UV-vis for our field assay. This

meant all H_2O_2 detection could be performed on site with minimal time between sampling and analysis. Samples were taken at both pools simulataneously and the samples for H_2O_2 analysis ferried to the analysis tent at each time point. Other measurements including Lux, Temperature, pH, ORP and Conductivity were performed at the pools in real time. Samples were also stored for returning to the UK for further analysis – Cations, Anions & Gasses.



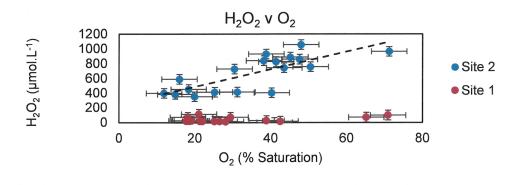
The main goal of our expedition was the measurement of H_2O_2 in an active geothermal system. We achieved this aim, measuring up to micromolar concentrations of H_2O_2 in one of our two sampling sites. The challenge now is to determine the source/mechanism of H_2O_2 generation. Our hypothesis before arriving was that seismic activity within the geothermal system would lead to rock-water reactions generating H_2O_2 .

H₂O₂ sensor data



Whilst we cannot yet discount this model of production (there were two $M_L \sim 1$ earthquakes withion 5 km of our site that appear to proceed peak H_2O_2 concentrations), we have also observed an apparent link between lux and H_2O_2 generation. Further, there are some samples/days where we measure a link between the oxygen levels in the liquids and H_2O_2 , although this may be due to the breakdown of H_2O_2 rather than driving its formation. We hope to be able to record any mixing of fluids through our laboratory analysis in the UK.

We will investigate all of this more closely once we have a more detailed picture of the seismic activity and have performed some experiments in our labs. This will provide a large dataset for us to interpret, and hopefully contain the key to unlocking the mystery of the source of H_2O_2 in Icelandic geothermal pools.



- Give details of any publications arising/planned (include conference abstracts etc)

We have at least 2 publications in mind for this fieldwork resulting directly from our field analyses in Iceland and the laboratory analysis we have/will perform back in the UK. We cannot be more specific until we have all of our laboratory data but are happy to keep Europlanet updated. Our field-based measurement of H_2O_2 at these concentrations in geothermal waters is unique. We will first submit the main manuscript to a top tier journal, hopefully by the years end, and see what the response is. Results will be taken to conference in 2024, likely the British Planetary Science Conference (BPSC) or the European Planetary Science Conference (EPSC).

- Host confirmation

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The host is required to approve the report agreeing it is an accurate account of the research performed.

Host Name	René Groben, Matís ohf.	
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<u>Date</u>	05.10.23	

- Project Leader confirmation

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Project Leader Name	John Owen Edgar
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<u>Date</u>	05/10/2023