Simulating water-rock reactions on the ocean floor of Enceladus. R. E. Hamp, D. Siggs, C. Batty, S. P. Schwenzer, K. Olsson-Francis and V. K. Pearson, AstrobiologyOU, Faculty of Science, Technology, Engineering and Mathematics, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom, rachael.hamp@open.ac.uk

Introduction: The subsurface of Enceladus is a potentially habitable environment, with a global subsurface ocean [1] and ongoing hydrothermal activity [2]. Geochemical reactions on Enceladus occur at the rock-water interface and reaction products are transported in the water column to the ice-ocean interface [2]. They are then ejected into space, *via* the plumes in the South Polar Region, and have been detected by instruments onboard the Cassini spacecraft [3-4]. The analysis of these plumes and the ice grains in the E-ring have provided information on the internal chemical and physical conditions on Enceladus [2-4], however owing to limitations on Cassini's instruments and limited understanding of plume formation processes, there are still many outstanding questions with regard to the internal environment of Enceladus.

Here, we present the results of preliminary experiments that simulate the interactions that take place at the ocean floor of Enceladus, which build on our previous efforts to model this environment [5-6].

Methods: We carried out water-rock reactions under simulated Enceladus conditions between a silicate simulant with a fluid of hypothesized initial Enceladus ocean composition, to study the compositional evolution to a modern-day ocean.

Silicate: We have assumed the silicate composition is that of a CI carbonaceous chondrite [7], based on the analysis of the ice grains within the E-ring and the plumes, and have used a bespoke simulant to represent this [7].

Ocean fluid: Our initial ocean fluid composition was derived from thermochemical modelling [6] and Cassini observations [3], and was comprised of the major species ($NaCl/NaHCO_3/Na_2CO_3/KCl$) at concentrations determined in our previous study [5-6].

Physical Conditions: The experiments were run at temperatures of 90, 120 and 150 ℃. These values were selected because: (i) 90 ℃ is the optimum temperature at which SiO_2 stream particles are proposed to form [2]; (ii) our previous thermochemical modelling [5-6] determined that temperatures 90-120 °C produced an ocean composition that was comparable to the ocean chemistry of Enceladus inferred from Cassini data; (iii) 120 °C is just below the highest temperature (121 °C) known for life to survive [8]; (iv) 150 °C provided an upper temperature limit to further explore the role of temperature.

The pressure hypothesized for the water-rock interface is 80 bar, based upon the combined depth of the subsurface ocean and ice crust, along with gravitational data [2]. Therefore, all of the experiments were carried out using this pressure.

Experimental Setup All simulations were carried out using static Parr reactor vessels (Figure 1) at The Open University Subsurface Simulation Laboratory. Two types of simulation were run. The first was batch non-sampling experiments, where the fluid and simulant were analysed at the end of a 21 day long simulation. The second was batch sampling experiments, where 5 mL aliquots of the fluid were taken twice a week throughout the 21 day experiment to track changes in chemistry over time. All experiments reacted ocean fluid (45 mL in non-sampling and 60 mL in sampling experiments) with a silicate simulant (15 g), and were heated and pressurized to the parameters previously described. The vessels were purged with nitrogen to remove any oxygen from the fluid, and the simulations carried out with a nitrogen headspace.

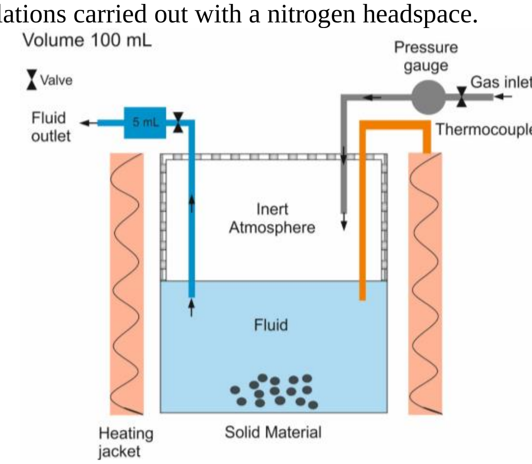

Figure 1 A schematic to represent our experimental set up for the water-rock simulation experiments using the Parr 4793 reactor. Reaction is carried out in 100 mL reactor heated through a heating jacket controlled by a thermocouple dipped into the experimental liquid.

Analysis The fluid was analyzed using ICP-OES, TC and TOC. The simulant was analyzed using SEM and EPMA. The headspace was analyzed using TD GC-MS.

Results/Discussions: *Non-sampling experiments:* All initial experiments (90 and 120 °C) produce fluid chemistries that are in agreement with data from Cassini, where the dominant chemical species observed were Na^+, K^+, CO_3^{2-}/HCO_3^- [3]. Further to this, the measured pH in both of these experiments was ~9, which agrees with current predictions for the pH of the modern day Enceladus ocean [9]. The fluid contained aqueous sulfur species, which are yet to be detected by Cassini, likely owing to their concentrations being below the limit of detection of the instruments. This sulfur originates from the dissolution of sulfide and sulfate minerals in the simulant. A wide range of trace aqueous species were also identified, which included metal ions such as Mg, Fe, Mn, and Ca, which have not been observed by Cassini.

Our initial findings show that the ocean fluid was more concentrated in the lower temperature (90 °C) experiment, which implies a greater dissolution of silicate material. This is supported through the post-experimental analysis of the simulant, where we see a larger alteration of silicate material at lower temperatures, which included a relative increase in the concentration of Si and Mg, and a decrease in Fe. At higher temperatures (120 °C) the converse holds true, with a more dilute fluid and a simulant with less alteration in comparison to the starting simulant, where the concentrations of Si, Mg, Fe, Ca remained consistent with the initial starting simulant. This suggests the higher temperature experiment resulted in less dissolution/alteration to the solid phase. The 150 °C experiment is currently ongoing.

Sampling experiments: Figure 2 shows the concentration of 6 fluid species across the 21 day experiment at 120 °C. It can be seen that these species followed a very similar trend where from day 0 to day 3 they increase in concentration, suggesting initial silicate dissolution. However, over the next 7 days there is a decrease in concentration, suggesting precipitation of solid phases from the solution. We hypothesise this dissolution and precipitation cycle will continue until an equilibrium between the two is reached (Figure 2).

The remaining temperature sampling experiments are ongoing and we anticipate these results will provide an insight into differences in the alteration observed in the fluids and simulant with temperature.

Overall, our study supports the concept that Enceladus is habitable by suggesting the ocean may be only mildly alkaline, and that aqueous sulfur may be present, completing the inventory of bio-essential elements (CHNOPS) that are evident in the Enceladus subsurface [3-4]. The formation of metal ions (e.g. Mg, Ca, Fe and Mn) also supports Enceladus' potential to be habitable, since such metal ions are essential for life based on our current understanding.

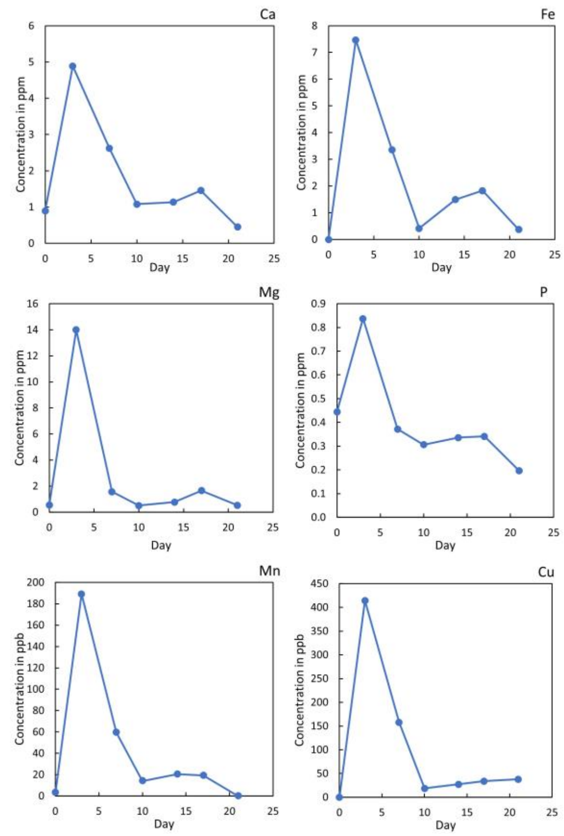

Figure 2 The change in concentration in the 120 °C experiment of a few example fluid species throughout the progression of the three week water-rock experiment. Showing the initial increase in concentration followed by a large decrease.

Summary: Our initial results show that the ocean fluid derived from our water-rock simulations is comparable to the major chemical characteristics of Enceladus's present day ocean, including the alkaline pH of ~9 and the abundance of salts and carbonates. Our work also adds to the current understanding of Enceladus by highlighting new species that have not yet been detected in the plumes, including sulfur and metal ions. This is also in agreement with our previous thermochemical modelling work [5-6].

Our initial study also finds that higher temperature reactions may undergo less chemical alteration than a lower temperature experiment, however this will be further investigated when we study higher temperatures.

References: [1] Thomas P. C. et al., (2016), *Icarus*, **264**, 37-47 [2] Hsu H. W. et al., (2015), *Nature*, **519** [3] Postberg F. et al., (2009), Nature, 459, 1098-110 [4] Waite et al., (2017), *Science*, **356**, 155-159 [5] Hamp et al., (2021), 52nd LPSC 2021, Abstract **2548** [6] Hamp et al., (2023), *GCA* (in rev) [7] Hamp R. E. et al., (2019), 50th LPSC 2019, Abstract **1091 [**8] Clarke A., (2014) *Astrobiology*, **13**, 141-154 [9] Glein, C. R and Waite, J. H., (2020) *GeoPhys Res Letts*, **47**