AN EXPERIMENTAL-MODELING APPROACH TO DETERMINE ENCELADUS' INTERIOR HYDROGEN GENERATION.

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Introduction: Recent models of the interior of Enceladus seem to agree that underneath the ice shell there exists a global ocean. Size estimates of this ocean vary from 21-63 km thick [1,2]. The details of the composition of this ocean are not immediately clear.

The plumes of Enceladus can provide us with a glimpse of what is happening in the interior. The latest analysis of Cassini data shows that H_2 makes up 0.4 to 1.4% of the total of Enceladus' plumes [3]. Analysis of the H_2/CH_4 ratio in the plume suggests that this H_2 must be actively generated [3]. While there are a number of geochemical reactions that can produce H_2, only some are considered to be of importance on Enceladus.

One such process for the major source of H_2 on Enceladus appears to be the aqueous alteration of minerals [3]. Models of these serpentinization reactions show that anywhere from $(0.4 - 6) \times 10^9$ kg of H_2 need to be produced each year to maintain the hydrogen levels observed in the plume [3]. Only as much as 40% of the core needs to have fully reacted to sustain the present level of hydrogen generation over the history of the Solar System [3].

Pyrolysis is an additional potential source of H_2 generation in Enceladus. However, current pyrolysis research regarding the production of H_2 has been limited to dry heating at high temperatures (350-800° C) for short amounts of time (minutes) [3]. It is therefore not straightforward to extrapolate the results to Enceladus or icy worlds in general, where pyrolysis may be occurring in an aqueous environment at lower temperatures (< 300° C) over much longer timescales.

While considerable attention has gone into understanding how geochemical reactions shape the rock and hydrogen production on Enceladus, seemingly less attention has been given to how these reactions impact the state of the ocean.

This work hopes to further quantify a possible ocean composition for Enceladus through both modeling and experimentation. Rather than focus on mineral composition and hydrogen production, modeling efforts will be focused on describing possible free ions, dissolved salts, and organic species found in the ocean. The experimentation portion will look at how pyrolysis is affected by a low temperature, hydrous environment. Composition of both the resulting liquid and produced gas will be analyzed.

Science Motivation: The prospect of active hydrogen generation is of great interest to those studying astrobiology, since hydrogen is a food source for microorganisms. The presence of not only liquid water but also a plentiful energy source makes Enceladus a great astrobiological target. In fact, Enceladus does seem to have all of the elements necessary for life [4]. To determine the likelihood of life surviving or thriving in Enceladus' ocean, however, we need to have a complete picture of the dissolved solids content, pH, temperature, and pressure of the ocean. This will allow us to understand the limitations placed on potential life in Enceladus.

Current predictions state that the pH of Enceladus' ocean is likely between 9-12 with some variation as to the range [3, 5, 6]. The narrowing of this pH range is not only beneficial to studies of astrobiological potential, but also to more extensive geochemical modeling.

Modeling Approach: To investigate ocean composition through geochemical modeling, this project makes use of the freely available geochemical modeling software *PHREEQC 3.3.12* [7]. To apply minerals/gases/aqueous species that are relevant to Enceladus, this modeling makes use of the *core10.dat* database, which was specifically designed by Neveu et al. [8] to model the geochemical interiors of icy worlds.

Initial core compositions were determined using a combination of the major rock types of Waite et. al. [3] and additional organics and trace elements as appropriate using the composition guidelines found in Neveu et al [8]. Previous works take into consideration the expected solar system elemental abundances as defined by Lodders [9], thus this idea is carried over into this work and parameters have been adjusted accordingly. The initial fluid composition is taken to be that of cometary composition containing primarily C, N, S, and Cl, such as described by Neveu et al [8].

For the purposes of this modeling, it is assumed that the ocean experiences complete mixing on reasonable timescales, meaning pore water and ocean water can freely mix with one another. It is also assumed that there is not significant melting of the overlaying ice sheet that would supply additional water to the ocean and thus change the concentrations.

Since it is likely that Enceladus' core is not yet fully reacted, care needs to be taken during the setup of the model. It is critical to not attempt to react more core material than is expected, as to do so will give an incorrect estimate of the current state of the ocean. To account for this, the model does the calculations in steps as follows:

1. The calculated density of the core does not allow for much, if any, remaining anhydrous accreted rock (AAR) [3]. Therefore, the entire initial mass, which we assume is primarily AAR with the organics/trace minerals included, can react fully into metamorphized anhydrous rock (MAR) and reduced hydrous rock (RHR) [3]. This is done by allowing only those minerals that we expect to see in MAR and RHR precipitate. Gaseous and aqueous species can dissolve and precipitate relatively unrestricted. The resulting solution, now called Solution 2, is then saved for use in the next step.
2. Since it is possible that Enceladus' core has fully reacted anywhere from 2-40% [3], the same percentages will be examined here. Mass percentages of the core will be chosen incrementally in the 2-40% range, and will then be reacted with Solution 2 and the gas phase from the first step. This new solution is now saved as Solution 3, and should be representative of the expected ocean composition of Enceladus.

While this model setup is simplified when considering the multitude of possible minerals that may actually form, it should still be possible to extract meaningful conclusions regarding the basic composition of Enceladus' ocean.

Experimental Approach: Low temperature pyrolysis experiments will be conducted at 100° C, 200° C, and 300°C using both sand and gravel sized carbonaceous chondrite samples. The variety of grain size will allow for a more complete understanding of how a hydrous environment affects pyrolysis. Each sample will be on the order of 1 g. Pure water will be added to the sample to achieve a W:R ratio of 1:2. For this experiment, the use of pure water allows for an uncontaminated look at the effect of a hydrous environment on the sample. Later experiments may include more complex aqueous solutions, such as approximated cometary fluid.

The reaction will take place inside a pressure vessel with an appropriate vent to avoid unnecessary buildup of excess pressure. This will help to channel the gas in a way through which the production rate can be measured and the gas can be collected for sampling. In order to track reaction progress, the rate of production will be noted and the gas will be sampled approximately every two hours. The composition of the extracted gas will be determined using gas chromatography. At the completion of the reaction, the composition of the liquid and remaining rock sample will be tested.

Upon completion of all experimental runs, the collected data will be analyzed and results will be used in conjunction with the modeling results in order to get a more complete understanding of the state of Enceladus' interior.

Discussion: The modeling-experimental approach for determining the processes involved via alterations and mineralogy leads to critical questions: (1) What is the lifetime of H_2 generation? (2) Is and was there disequilibrium? (3) Could more than one process be involved in the serpentinization? (4) Is serpentinization regarded as a global phenomenon or regional to Enceladus? (5) Do tectonic forces inhibit or destroy evidence of certain processes? (6) Are there chemical signatures of biology in the plumes? These and other key questions can be eventually resolved by careful in situ chemical and mineralogical measurements.

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