Exploring the Oxidation Chemistry of Enceladus' Ocean.

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Introduction: The detection of molecular hydrogen in the plume of Saturn's icy moon Enceladus implies that there is positive chemical affinity (i.e., free energy available) for methanogenesis, the metabolic reaction of hydrogen with carbon dioxide to form methane and water [1]. Methanogenesis, however, is just one of many possible metabolic pathways that could be utilized by putative microorganisms. While reduced species are abundant in the plume, CO_2 was the only oxidant observed.

Approach: To constrain the amount of metabolically important oxidants including sulfate (SO_4^{2-}), molecular oxygen (O_2) and ferric iron (for which we choose FeOOH as representative of ferric oxyhydroxides) in Enceladus' ocean, we present a geochemical model of the ocean based on detections made by the Cassini INMS instrument [1] and likely equilibrium mineralogies of Enceladus' core. We use a model of radiolysis on the surface of Enceladus to estimate the amount of molecular oxygen contained in the ice, and calculate the delivery rate of O_2 from the surface ice to the ocean using previous estimates of the rate of ice deposition on the south polar region [2]. Assuming this activity has occurred over ~4.5 billion years, we obtain an upper limit of $\sim 10^{16}$ moles of O_2 delivered to the ocean over Enceladus' lifetime. We also consider O_2 produced radiolytically in the ocean from electrons and gamma rays released by the decay of ^{40}K atoms. We calculate an upper limit of another $\sim 10^{16}$ moles of O_2 produced this way, from the inferred ^{40}K concentration in Enceladus' ocean (based on [3] and [4]) and rate equations for radiolytic reactions in primitive ocean waters from [5].

Results and discussion: The produced oxygen could react with sulfides and ferrous iron dissolved in the ocean to produce SO_4^{2-} and FeOOH, respectively. We estimate upper limits on the concentrations of these species from the solubilities of a number of possible ocean floor minerals, calculated using Geochemist's Workbench [6]. We find that the abiotic oxidation of these species could yield a dissolved sulfate concentration as high as 1.75 mmol/(kg H_2O), and a ferric iron bulk concentration as high as 0.55 mmol/(kg H_2O).

We determine the amount of chemical energy that could be available from metabolic reactions involving O_2, SO_4^{2-} and FeOOH reacting with reductants such as molecular hydrogen, sulfides, ferrous iron and hydrocarbons, and compare it with the energy available from methanogenesis reported in [1]. From these results, we suggest that that these oxidation reactions could provide an important additional source of chemical energy available for possible life, unless Enceladus is much younger than the age of the solar system or if the plume has been far less active over the course of its lifetime than what is presently observed. Finally, we consider how the production of oxidants from radiolysis of pore water in the core, and how the abiotic consumption of oxidants by reduced minerals in the core, could affect the reported results.

References: [1] Waite et al. (2017) *Science, 356,* 155–159. [2] Kempf et al. (2010) *Icarus, 206,* 446-457. [3] Postberg et al. (2009) *Nature, 459,* 1098–1101. [4] Lodders, K. (2003) *ApJ, 591*, 1220-1227. [5] Draganic et al. (1991) *Precambrian Res, 52,* 337-345. [6] Bethke, C. M. and Yeakel, S. (2018) *Geochemist's Workbench Essentials Guide*, Aqueous Solutions, LLC, Champaign, Illinois.