

**THE CHEMISTRY OF ENCELADUS' OCEAN FROM A CONVERGENCE OF CASSINI DATA AND THEORETICAL GEOCHEMISTRY.** C. R. Glein<sup>1,2</sup>, J. A. Baross<sup>3</sup>, J. H. Waite Jr.<sup>4</sup>, <sup>1</sup>Geophysical Laboratory, <sup>2</sup>Dept. of Earth Sciences, Univ. of Toronto (chris.glein@utoronto.ca), <sup>3</sup>Astrobiology Program and School of Oceanography, Univ. of Washington (jbaross@u.washington.edu), <sup>4</sup>Southwest Research Institute (hwaite@swri.edu).

**Introduction:** Saturn's icy satellite Enceladus is strongly suspected of possessing a subsurface ocean of liquid water below its geologically active south polar region [1-5]. The ocean is thought to be the source of chemicals in Enceladus' plume [3,4]. The composition of the ocean is of great interest, as it contains key clues to the geochemical evolution of Enceladus [6], it sets the boundary conditions for possible living processes inside Enceladus [7], and it can serve as a model for understanding the potential ocean chemistries and astrobiological potential of other icy worlds [8] that may not be erupting free samples into space. With the end of the *Cassini* mission in sight, we seek to maximize the existing data to constrain the geochemistry of Enceladus' ocean as much as possible to help prepare for the next generation of Enceladus exploration.

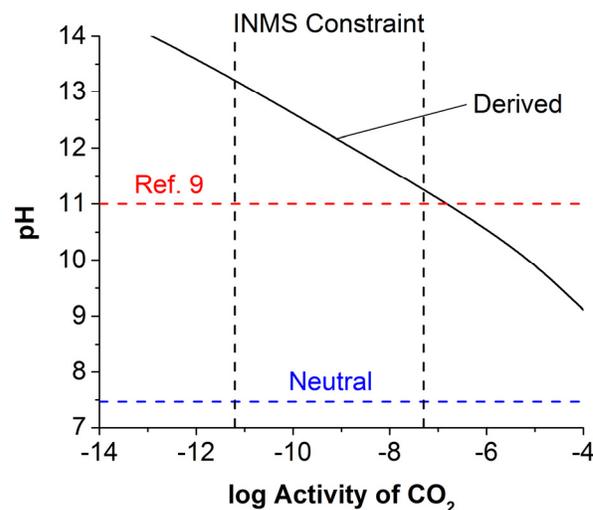
There are significant gaps in our understanding of the chemistry of Enceladus' ocean. [9] developed a theoretical model of chemical equilibrium between water and chondritic rock, and predicted the pH and concentrations of major chemical species in the ocean. However, this model was developed before the chemistry of the plume was characterized in detail [3,4], so the model could not be constrained by observational data. Here, we use *Cassini* CDA and INMS data to develop the first top-down (observationally constrained) model of the chemical composition of Enceladus' ocean [10]. We then take a bottom-up theoretical approach in an attempt to explain the derived composition in terms of simple geochemical equilibria.

**Top-down model:** Consistent with prior work [1-4], we assume that the plume gases and ice grains are derived from a subsurface ocean. In this model, the gases are generated by the degassing of ocean water at low-pressure interfaces where the tiger stripe fractures intersect the ocean, and the salt-rich grains represent ocean water that is flash-frozen during the eruption process. We focus on the Na-Cl-C-N-O-H chemical system, and calculate the composition of ocean water that would yield plume gas and ice grain compositions consistent with those reported by [11] and [3], respectively. The composition of the plume gas is updated from [4] based on more recent, slower flybys that provide data that more closely reflect the unmodified composition of the plume. We account for a distillation effect that concentrates volatile species in the plume gas relative to the source region, as a consequence of the removal of water vapor by condensation while the warm vapor travels through colder fractures [2, 10].

These considerations allow us to transform the observational data into a set of constraints that can be coupled to geochemical speciation calculations that are performed using the Geochemist's Workbench [12].

**Top-down results:** From the measured composition of the plume gas [11], we set an upper limit of  $\sim 0.01$  for the activity of  $\text{NH}_3$ , and we find that the activity of  $\text{CO}_2$  should fall in the range  $10^{-11.2}$ - $10^{-7.3}$ . These values are not more specific because of uncertainties in modeling the distillation effect [10]. Nevertheless, they provide valuable insights into the chemistry of Enceladus' ocean. The  $\text{NH}_3$  activity is approximately equal to its molality ( $m$ ). The upper limit is interesting because, based on observations of comets [13], we might expect the concentration of primordial  $\text{NH}_3$  to be  $\sim 0.1$ - $1 m$ , or even higher if the eutectic mixture is present. It is possible that Enceladus accreted "warm" ices that were depleted in  $\text{NH}_3$ , but this would be inconsistent with the elevated D/H in water [4]. Instead, the "missing"  $\text{NH}_3$  may have been removed by past outgassing, hydrothermally oxidized to  $\text{N}_2$  [6], or incorporated into organic or biomolecules [4,7].

By constraining the  $\text{CO}_2$  activity, we can estimate the carbonate speciation and pH of the ocean [10].



**Fig. 1.** The pH of Enceladus' ocean from a nominal geochemical model ( $0^\circ\text{C}$ ,  $0.2 m \text{ Cl}^-$ ,  $0.07 m \text{ C}_{\text{inorg}}$  [3]).

The Enceladus ocean should have a basic pH of  $\sim 12$  (Fig. 1). A more complete analysis that accounts for the uncertainties gives  $\text{pH} = 12.2 \pm 1.4$  [10]. Evidently,

Enceladus' ocean is substantially more basic than terrestrial seawater ( $\text{pH} \approx 8.1$ ), but the pH is similar to those measured in waters ( $\sim 9$ - $12.5$ ) from low-temperature serpentinization environments on Earth, such as the Oman ophiolite [14]. This implies that serpentinization has been an important process in controlling the pH of Enceladus' ocean, consistent with the predictions of [9]. Widespread serpentinization of chondritic rock can also explain the low density of Enceladus' rocky core [5], which is similar to that of serpentine ( $\sim 2.5$  g/cc). The inferred occurrence of serpentinization has profound astrobiological implications, because serpentinization leads to the production of  $\text{H}_2$  [15], which can drive the synthesis of organic compounds, and  $\text{H}_2$  can be metabolized to provide energy for life. If serpentinization is occurring today, then the Enceladus ocean should be habitable to some microorganisms, notably methanogens [7,10].

**Bottom-up model:** We explore whether the pH and other compositional characteristics of Enceladus' ocean can be buffered by an assemblage of alteration minerals on the ocean floor [9,16]. To simplify the problem, we consider the system: Na-K-Cl-Br-Mg-Ca-Si-C-N-O-H, and neglect the roles of redox and organic reactions that are unlikely to be governed by chemical equilibrium at  $0^\circ\text{C}$ . The model accounts for all of the major elements with the exceptions of Fe, S, and Al. The geochemistry of Al is very complex at low temperatures because clay minerals are compositionally diverse, which makes it difficult to provide a realistic thermodynamic representation. We treat minerals as the pure endmembers, and compute chemical equilibrium using the Geochemist's Workbench [12].

**Bottom-up results:** We constructed activity diagrams to determine the stability relations of minerals in the model system, and we also consulted the meteoritics literature to gain insights into how serpentinization can alter the mineralogy of chondritic rock [17]. Based on these considerations, we found that a mineral assemblage of serpentine-talc-calcite-dolomite-gaylussite in equilibrium with liquid water at  $0^\circ\text{C}$  can provide a close match to the composition of the Enceladus ocean that was derived from the top-down model. Talc can be viewed as an endmember proxy for more complex trioctahedral, Al-bearing saponites [17]; and the presence of gaylussite (a Na-Ca carbonate) would be consistent with the high carbonate concentration [3], which may result from accretion of  $\text{CO}_2$ -rich ices [13].

This model is interesting in that the only independent compositional variable is the chlorinity. Once that is specified, the bulk composition and speciation of the ocean are fixed, as required by the phase rule [16]. For a nominal chlorinity of  $0.2$  m, we calculate a pH of 11.4, consistent with the top-down model (Fig. 1) and

[9]. The predicted pH decreases with increasingly chlorinity, but it is not a sensitive function; a plausible chlorinity range of  $0.05$ - $1.2$  m [10] yields a pH range of  $10.9$ - $11.5$ . The ocean is predicted to be a saline water dominated by  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{CO}_3^{2-}$ , consistent with CDA observations [3]. Table 1 summarizes the results. Overall, the "serpentinization buffer" provides an appealing explanation of the available data [3,11].

**Table 1.** Computed composition of Enceladus' ocean.

Element	Concentration ( $\mu\text{m}$ )
Na	340,000
Cl	200,000
Inorganic C	73,000
K	3300
Reduced N	1100
Br	430
Si	220
Ca	5
Mg	0.5

**Conclusions:** Based on the convergence of observational and theoretical data, we conclude that (1) Enceladus' ocean should have a pH of 11-12; and (2) serpentinization is the key process that dictates the inorganic chemistry of Enceladus' ocean [10]. This leads to a new set of critical questions, including (1) Is  $\text{H}_2$  being generated today? (2) How much chemical disequilibrium is present inside Enceladus? and (3) Are there chemical signatures of biology in the plume? These and other key questions can be resolved by making sensitive in situ chemical and isotopic measurements of the plume, as proposed by the *Enceladus Life Finder* (ELF) Discovery mission candidate [18].

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