### Contribution of Non-Water Ices to Salinity and Electrical Conductivity in Ocean Worlds

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#### Abstract

Modeling of the electrical conductivity (EC) of icy moon oceans has previously assumed that chloride, sulfate, and other ions released from rock leaching are the main solutes and carriers of electrical conductivity. Here, we show that accreted volatiles, such as carbon dioxide and ammonia, can add a significant fraction of solutes in bodies whose volatile content was in part supplied from cometary materials. These volatiles can increase the EC of aqueous solutions above 1 S/m. Our salinity and EC estimates can serve as a basis for planning future magnetometer investigations at icy moons and dwarf planets. In particular, oceans expected in some of the Uranian satellites and Neptune's satellite Triton could have EC above 3 S/m as a result of accretion of large abundances of carbon dioxide and ammonia, even if rock leaching during water-rock separation was limited, and chlorine and sulfur abundances may be at CI carbonaceous chondritic levels.

# Contribution of Non-Water Ices to Salinity and Electrical Conductivity in Ocean Worlds

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#### 7 Key Points:

8 9	•	Accreted CO <sub>2</sub> and NH <sub>3</sub> can significantly increase the salinity and electrical conductivity of deep oceans
10 11	٠	Water to rock ratio and ammonia abundance drive the concentrations of carbonate and bicarbonate ions in solution
10	_	Design to the state of the stat

Predicted electrical conductivity estimates can be used to plan future ocean search
 missions at icy moons and dwarf planets

#### 15 Abstract

Modeling of the electrical conductivity (EC) of icy moon oceans has previously assumed that 16 chloride, sulfate, and other ions released from rock leaching are the main solutes and carriers of 17 18 electrical conductivity. Here, we show that accreted volatiles, such as carbon dioxide and ammonia, can add a significant fraction of solutes in bodies whose volatile content was in part 19 supplied from cometary materials. These volatiles can increase the EC of aqueous solutions above 20 1 S/m. Our salinity and EC estimates can serve as a basis for planning future magnetometer 21 investigations at icy moons and dwarf planets. In particular, oceans expected in some of the 22 23 Uranian satellites and Neptune's satellite Triton could have EC above 3 S/m as a result of accretion of large abundances of carbon dioxide and ammonia, even if rock leaching during water-rock 24 25 separation was limited, and chlorine and sulfur abundances may be at CI carbonaceous chondritic 26 levels.

#### 27 Plain Language Summary

28 Searching for deep oceans in icy bodies is a major driver of planetary exploration. Magnetometry 29 is used to detect electric current in deep oceans generated by a varying magnetic field, from a giant planet or solar wind, as Galileo did at Jupiter's moon Europa. Previous studies have assumed that 30 the salinity of deep oceans is determined by the leaching of major elements from accreted rock, 31 which generally yields brackish and low electrical conductivity solutions. We show that carbon 32 33 dioxide, an abundant ice in the outer solar system, could contribute a significant fraction of solutes 34 (carbonate and bicarbonate ions) in ocean worlds, regulated in particular by the presence of ammonia. The latest solar system dynamical models predict that dwarf planets and most icy moons 35 accreted ices rich in carbon dioxide and ammonia. Hence, carbonate-rich oceans in these bodies 36 37 may display a magnetic signature detectable by future spacecraft missions.

38

#### 39 **1 Study Motivation**

The detection of induced magnetic fields has proven to be the most definitive approach to detecting water oceans in icy bodies (e.g., Khurana et al. 1998; Zimmer et al. 2000). In general, the magnetic field characteristics depend on the combination of the ocean thickness and electrical conductivity (EC). The electrical conductivity is an important parameter because it is related to the ocean's salinity (Vance et al. 2021). Salinity is defined as the mass of dissolved solids per kilogram of water. Note that only dissolved ions contribute to the solutions' conductivity. Knowledge of salinity can help to constrain both the habitability and geochemical evolution of ocean worlds.

47

48 The classical approach is to assume that ocean salinity is dominated by constituents that were

- 49 leached from rock. This leads to endmember compositions of NaCl or MgSO<sub>4</sub> (e.g., Hand et al.,
- 50 2007; Vance et al. 2020). However, it is increasingly evident that volatiles can play a larger role
- in the ionic chemistry of ocean worlds than previously considered.  $CO_2$  and (bi)carbonate ions are
- 52 major species in a plume sourced from the subsurface ocean of Enceladus (Postberg et al., 2009;

53 Waite et al., 2017). Glein and Waite (2020) emphasized the important role played by carbonate in

that moon's chemistry. Carbonates have also been suggested as contributors to the salinity of

55 Europa's ocean (e.g., Zolotov and Shock 2001). The most abundant primordial (e.g., cometary) 56 species that can directly produce carbonates in liquid water environments is CO<sub>2</sub>. While organic

species that can directly produce carbonates in liquid water environments is CO<sub>2</sub>. While organic carbon oxidation can also generate CO<sub>2</sub> for carbonate formation, high  ${}^{13}C/{}^{12}C$  ratios of carbonates

- in carbonaceous chondrites implicate  $CO_2$  ice as a significant source of carbonate carbon (Fujiya
- 59 et al., 2019). In this respect, it is relevant that  $CO_2$  has been observed on the surface of Triton
- 60 (Cruikshank et al., 1993).
- 61
- Ammonia is another cometary volatile that has affected the chemistry of ocean worlds. Enceladus' 62 plume gas contains NH<sub>3</sub> (Waite et al. 2017). There is spectroscopic evidence for the presence of 63 some form of ammonia on Pluto's surface (Dalle Ore et al. 2019). The low <sup>14</sup>N/<sup>15</sup>N ratio of Titan's 64 atmospheric N<sub>2</sub> indicates that ammonia was accreted and participated in early chemical processes 65 (Mandt et al. 2014). Some of this ammonia could still exist in Titan's subsurface ocean, but in the 66 form of ammonium salts. A source of dissolved species beyond those that would be released from 67 rock is apparently needed. Salinity estimates for Titan's ocean may be derived from the inversion 68 of the tidal Love number  $k_2$  (e.g., Durante et al. 2019). However, estimates so far suggest high 69 ocean densities, up to 1350 kg/m<sup>3</sup>, at the base of the ocean (accounting for pressure). On the other 70 hand, modeling of the ocean salinity as a result of leaching of major elements from rock yields a 71 salinity of ~1 wt.% (Leitner and Lunine 2019), or a fluid density of ~1200 kg/m<sup>3</sup> at the base of the 72 ocean. Brasse et al. (2017) emphasized that Titan's ocean could be an ammonium-carbonate-73 74 bearing system, which is also the case for Ceres (Castillo-Rogez et al. 2018; Raponi et al. 2019). Carbon dioxide and NH<sub>3</sub> have been found on several of the Uranian moons in association with 75 geological features (e.g., Cartwright et al. 2020 and references therein), which supports an 76 endogenic origin. 77
- 78

The combination of CO<sub>2</sub> and NH<sub>3</sub> in water is of special relevance, as these species react with each other and water to produce predominantly dissolved ammonium bicarbonate in moderately alkaline environments hosted by ocean worlds (Kargel 1992; Zolotov 2007; Castillo-Rogez et al. 2018) (see Figure S1) via

83

84 
$$NH_3(aq) + CO_2(aq) + H_2O(l) \rightarrow NH_4^+(aq) + HCO_3^-(aq).$$
 (1)

85

The potential to produce ions from non-water ices is not a new topic of research; however, little systematic work has been done on the contribution of solutes derived from accreted ices to EC values. Thus, our current understanding of the links between ocean composition, salinity, and EC is incomplete.

90

91 Here, we quantify the impact of major volatiles on the salinity and EC of ocean worlds in support

of future electromagnetic field investigations at these bodies, as currently planned for, e.g., JUpiter

93 ICy moons Explorer and Europa Clipper, and under consideration for missions to the icy giant

systems and Ceres. The whole geochemical system is considered, not just rock leaching or the

95 CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O ternary. Water-rock interactions and the fate of accreted volatiles are all tracked

together. We perform geochemical modeling (Section 2) to derive salinity for a range of plausible

- 97 compositions and environmental conditions prior to concentration as a consequence of ice shell
- 98 freezing (Section 3). Implications for future observations are addressed in Section 4.

#### 99 2 Materials and Methods

We assess the fate of primordial volatiles in oceans using the *Geochemist's Workbench* (GWB) (Bethke 2007) and especially the React application, building on previous work (Castillo-Rogez et

- al. 2018; Glein and Waite, 2020). GWB is a commercial suite of geochemical modeling tools. It 102 uses databases of thermodynamic equilibrium constants to determine chemical equilibrium of 103 solutions that may involve a variety of volatiles. GWB can describe a wide range of conditions 104 relevant to ocean worlds. However, the default pressure of 1 atm. Pressure effects on aqueous 105 equilibria from 1 to 5000 bar were found to be insignificant compared with variation caused by 106 other parameters (see Figure S2 for an example). We use a temperature of 0°C, which corresponds 107 to the melting temperature of pure water ice. To first order, this is appropriate because oceans in 108 the outer solar system are covered by ice. Generalized conductivity models (see below) do not 109 exist at sub-zero temperatures. We use the thermo.com.V8.R6+ thermodynamic database that is 110 largely based on the database used by SUPCRT92 (Johnson et al., 1992). It contains the volatile 111 compounds of interest as well as broad ranges of minerals, aqueous inorganic species, and organic 112 compounds. 113
- 114

115 GWB computes electrical conductivity using the approach by McCleskey et al. (2012), which is

suitable for ionic strengths up to 0.7 mol/kg over relevant ranges of temperature (0–95 °C), pH (1–

117 10), and conductivity (0.03–7 S m<sup>-1</sup>). The empirical relationships (EC as a function of temperature

and ionic strength) at the basis of this method were derived from conductivity measurements

119 obtained for ~30 electrolytes over a wide range of conditions. The equations were then coupled to

a geochemical speciation model. McCleskey et al. (2012) found that the predicted conductivity is

121 accurate to within  $\pm 5\%$  of measurements.

122 Key parameters driving the evolution of the system are (1) volatile concentrations; (2) the bulk

- 123 chemistry of rock; and (3) the extent of aqueous alteration of rock.
- 124

125 The initial volatile composition of ocean worlds depends on an object's accretional environment.

Assuming that comets are relatively pristine remnants of outer solar system building blocks, the

127 process of accretion implies that the initial volatile composition of larger solid bodies is likely to

- be of cometary nature (e.g., Triton, Shock and McKinnon 1993). In the case of the Jovian satellites,
- the origin of their volatiles is not well constrained, but could have been sourced from a reservoir
- 130 of planetesimals between Jupiter and Saturn (Batygin and Morbidelli 2020). We consider cometary
- volatile abundances from the review by Mumma and Charnley (2011) as a standard reference.

- However, no single composition can be adopted because comets are compositionally diverse. We focus on  $CO_2$  and  $NH_3$  in this work because they are the most abundant cometary volatiles that
- 134 can easily participate in acid-base reactions that affect electrical conductivity (see Section 3 for
- other volatiles). The concentration of  $CO_2$  in comets can be > 20 wt.% relative to  $H_2O$  (e.g.,
- 136 Ootsubo et al. 2012). Ammonia abundances measured at comets are <1.5 wt.%. However, the
- recent discovery of ammonium salts in comet 67P/Churyomov-Gerasimenko (Altwegg et al. 2020;
- Poch et al. 2020) and comets in general (Mumma et al. 2019) indicate that potentially a greater
- amount of  $NH_3$  condensed in planetesimals. The exact abundance of ammonium salts in comets is
- not well constrained but estimated to be a few percent (Poch et al. 2020) to 5–10 wt.% of the rocky
   material (Mumma et al. 2019). We capture much of the reported variability and current uncertainty
- material (Mumma et al. 2019). We capture much of the reported variability and current uncertainty by varying the amount of  $CO_2$  input to the system from 0 to 10 wt.% and that of NH<sub>3</sub> from 0 to 5
- 143 wt.%.
- 144

The adopted rock composition is based on the elemental composition of CI carbonaceous chondrites (without organic matter) (see Castillo-Rogez et al. 2018 for more detail on input to GWB). These objects are thought to be relevant to bodies formed beyond Saturn's orbit (Desch et al. 2018). A canonical abundance (680 ppm) of chlorine is included in the model rock (after Wasson and Kalleymen 1988 and consistent with Lodders 2021).

150

We use water/rock ratio (W/R) to represent reaction progress. It is defined as the initial fluid over 151 reacted rock mass ratio (e.g., Seyfried and Bischoff 1981). One can think of the ocean system as 152 initially being all fluid. As more of the rock inventory equilibrates with the fluid, W/R decreases. 153 In the limit of total equilibrium, the model's W/R converges to the bulk W/R. This path toward 154 chemical equilibrium is presumed to begin during ice melting that enables differentiation, and may 155 continue at later times via circulation of ocean water below the seafloor. The W/R for ocean worlds 156 is not well constrained because the internal evolutionary processes that control it are inadequately 157 understood. As an example, the relevant W/R for differentiation depends on the timescale for rock 158 particles to separate from volatile materials and settle into a rocky core. If this timescale is short 159 relative to the kinetics of mineral dissolution reactions, then only a small fraction of the soluble 160 components may end up in solution. Large particles (millimeters to centimeters) such as 161 chondrules may gravitationally settle from the water column faster and be only partially altered, 162 whereas fines (10s of µm) may remain in suspension for longer and be pervasively altered (Bland 163 and Travis 2017). The depth of circulation of ocean water into the rocky core depends on the 164 lifetime of the ocean, the permeability of underlying rocks, and the thermal evolution of the core. 165 In large icy moons (Triton, Europa, etc.), the faster sinking of rock particles due to higher gravity 166 and the decreased permeability of the seafloor due to higher pressure could limit the extent of 167 interaction between water and rock. It is difficult to determine how all of these processes come 168 together to yield a globally representative W/R, although past studies can provide some guidance. 169 Castillo-Rogez et al. (2018) derived a W/R $\gtrsim$ 3 to explain Ceres' surface mineralogy. Sekine et al. 170 (2015) assumed W/R=4 for Enceladus, per analogy with terrestrial submarine environments. Glein 171

- and Waite (2020) estimated a somewhat lower W/R (~0.85–2.8) for Enceladus from Cassini data.
- 173 Zolotov's (2012) study of aqueous alteration in CI chondrite parent bodies (with pressures up to
- 174 200 MPa) focused on W/R $\leq$ 2. Similarly, we expect low W/R overall but compute results for W/R
- 175 between 1–500.
- 176

A few simplifications are made based on our current knowledge of higher order issues and other 177 modeling limitations. First, a potential caveat of our approach is that magnesite (MgCO<sub>3</sub>) and 178 dolomite  $(CaMg(CO_3)_2)$  are allowed to form in these chemical equilibrium models. The formation 179 of these carbonates is kinetically controlled at temperatures lower than 60 °C (e.g., Zhang et al. 180 2000; Power et al. 2019). Temperatures in the early oceans of large water-rich bodies were likely 181 lower, at least during the differentiation phase, due to cooling via active hydrothermal convection 182 (e.g., Bland and Travis 2017). Metastable hydrated carbonates likely initially formed instead, such 183 184 as hydromagnesite and lansfordite. On the other hand, magnesite can precipitate over timescales of a few hundred thousand years, much shorter than the ocean lifetimes (>100 m.y.) of large water-185 rich bodies (Power et al. 2019). Many parameters come under consideration, such as pCO<sub>2</sub>, 186 nucleation and degree of saturation (e.g., in pores). Here, we consider that magnesite and dolomite 187 could form and also consider the consequences of inhibiting their formation in Figure S6. Both 188 minerals have been found in abundance on Ceres (Palomba et al. 2019). Magnesium-rich 189 carbonates have also been found in a variety of carbonaceous chondrites (e.g., Tagish Lake, 190

- 191 Nakamura et al. 2003) that experienced shorter phases of aqueous alteration.
- Another simplifying assumption is that the low temperature reaction kinetics are too slow for appreciable concentrations of hydrocarbons (e.g.,  $CH_4$ ) to form from  $CO_2$  (or CO) equilibria with
- appreciable concentrations of hydrocarbons (e.g.,  $CH_4$ ) to form from  $CO_2$  (or CO) equilibria with water and molecular hydrogen (Shock and McKinnon 1993). Similarly, we assume that the ocean
- 195 temperature is too low for molecular nitrogen to form from the decomposition of ammonia
- 196 (Matson et al. 2007). Should any of these processes occur, then the consequence would be similar
- 197 to assuming lower concentrations of  $CO_2$  and  $NH_3$  to start with. Ammonium may also be removed
- 198 from the system via exchange with cations (especially  $K^+$  and  $Na^+$ ). The consequences of that
- 199 exchange are addressed in Section 3.
- Lastly, we restrict our quantitative analysis to 1 atm total pressure, as the effects of pressure on the
- 201 electrical conductivity of aqueous solutions is presently insufficiently parameterized at higher
- 202 pressures (see Supporting Information for other details).

#### 203 **3 Results**

- Results for five different volatile abundances are presented in Figures 1–2 and S3 for the salinity and EC as a function of accreted (i.e., initial) concentrations of  $CO_2$  and  $NH_3$ , as well as water to
- rock ratio. These compositions were chosen to illustrate the various effects acting on the system.
- 207 rock ratio. These compositions were chosen to illustrate the various effects acting on
- A broader range of compositions is explored later on.
- 209

- 210 If ocean salinity is a sole function of fluid-rock reaction under equilibrium conditions, then the
- salinity should be on the order of 0.1-0.2 wt. %, consistent with previous modeling (e.g., Leitner and Lunine, 2019), yielding an EC ~0.2 S/m (black diamonds in Figure 1).





Figure 1. Effect of the water to rock ratio (W/R) on (a) salinity and (b) electrical conductivity (EC) for several accreted volatile compositions and  $log_{10}$  pH<sub>2</sub> (bar) = 2. Salinity is defined as the mass of dissolved salts per kilogram of solution. Dashed lines show the salinities and ECs obtained for solution based on accreted volatiles only, i.e., with no rock present. The latter results do not depend on W/R. (c) represents EC as a function of salinity of the covered space of parameters.

221

222 The presence of  $CO_2$  affects solute speciation in the NH<sub>3</sub> system, and vice versa. For example, dissolved CO<sub>2</sub> increases the acidity of the solution, which in turn determines whether accreted NH<sub>3</sub> 223 remains predominantly in this form, or NH<sub>4</sub><sup>+</sup> becomes another important source of ions to the 224 ocean (see Figure S1). If a small amount ( $\leq 2 \text{ wt.}\%$ ) of CO<sub>2</sub> (and no NH<sub>3</sub>) is added to the solution, 225 it would be sequestered to form dolomite and magnesite with little contribution to salinity (less 226 than [Na<sup>+</sup>] and [Cl<sup>-</sup>], see Figures S4, S5) unless these minerals cannot form over the lifetime of the 227 ocean. Figure S6 shows the difference in salinity and EC obtained when magnesite and dolomite 228 are suppressed from the system to reflect kinetic limitations (calcite and hydromagnesite form 229 instead) and when these minerals are allowed to form. The difference is particularly significant for 230  $[CO_2] < 3$  wt.% and  $[NH_3] < 1$  wt.%. Then, the salinity and EC remain  $\ll 1$  wt.% when no carbonate 231 is suppressed while these parameters can reach 2 % and >1 S/m, respectively, when magnesite and 232 dolomite are suppressed. A factor two difference between the results is found for [CO<sub>2</sub>] between 233 3–7 wt.% and low [NH<sub>3</sub>]. For higher [NH<sub>3</sub>], the salinity and EC are generally similar for the two 234

- types of models. For the rest of this paper, we assume equilibrium is reached for the reasons notedin Section 2.
- 237
- 238 The fraction of bi/carbonate ions in solution increases with increasing [NH<sub>3</sub>] (Figures 1–2, S3), as
- ammonia provides a charge-balancing cation ( $NH_4^+$ ). To further illustrate the contributions of  $CO_2$
- and NH<sub>3</sub> to the system, we compute the salinity and EC of endmember mixtures without rock
- 241 (Figure 1). These simulations almost systematically lead to salinities and EC that are higher than
- their counterpart with rock. This is because carbonate ions are removed to form carbonate minerals
- 243 if reactant rock is added.



Figure 2. Concentrations of the main solutes obtained for three different solutions introduced in Figure 1 for (Top) W/R = 10 and (Bottom) W/R = 1. This figure shows  $HCO_3^-$ ,  $CO_3^{2-}$ , and  $NH_{4^+}$  are the main contributors to salinity by up to one order to magnitude more than Cl<sup>-</sup>, alkali, and alkaline earth metals. See also Figure S4 for a summary of mol fraction for each class of solutes and Figure S7 for concentrations obtained for W/R = 100. Off-scale data points correspond to a molality very low or even equal to zero.

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The W/R ratio increases salinity significantly when high abundances of CO<sub>2</sub> and NH<sub>3</sub> are accreted. 251 252 The molality of  $HCO_3^-$  increases by one order of magnitude (15x) when W/R increases from 1 to 10, while the  $CO_3^{2-}$  molality decreases by two orders of magnitude (350x) over that range. For 253 W/R = 10, inorganic carbon is sequestered by magnesite, dolomite, and siderite (FeCO<sub>3</sub>) (Figure 254 S5), yielding six times as much carbonate precipitates than in the lower W/R case. Overall, for low 255 abundances of CO<sub>2</sub> and NH<sub>3</sub> (1 wt.%, 0.3 wt.%, respectively in Figure 1), the salinity is  $\leq 1$  wt.% 256 and EC  $\leq 1$  S/m for W/R < 20. For higher abundances of accreted CO<sub>2</sub> (5 wt.% cases in Figure 1), 257 the salinity increases sharply for W/R > 5 and yields an EC > 5 S/m. 258

259

Another finding, presented in Figure 2, is that at low W/R (= 1), the relative abundance of each solute remains about the same for the three compositions. On the other hand, for the high W/R example (W/R = 10), the solution speciation varies significantly. Figure S7 shows that the speciations obtained at W/R of 10 and W/R of 100 are similar. A high initial [CO<sub>2</sub>] increases the dissolved concentrations of Na+, K+ and Mg2+ as a consequence of increased acidity (Figure 1a) destabilizing the mineral sinks of these cations. For example, the concentration of K<sup>+</sup> decreases by three orders of magnitude if [CO<sub>2</sub>]<sup>1</sup> decreases from 5 to 1 wt.%.

267

We also test the effect of the partial pressure of  $H_2$  (redox conditions) on the results. We find that results remain almost constant over a range of partial pressures of  $H_2$  relevant to ocean worlds, between -3 and +2 on a  $log_{10}$  scale (e.g., McKinnon and Zolensky 2003). Observations at Enceladus support reducing ocean conditions based on the presence of  $H_2$ , CH<sub>4</sub>, organic compounds, and the lack of detection of sulfate salts in the plume (Ray et al. 2021).

The difference in salinity and EC between the two for the range of conditions covered in Figure 1 is <10 % and <2 %, respectively, in the majority of cases (Figure S8).

275

The solutions modeled in this study did not produce any sulfate in solution (Figures 2, S4, and S7), which is expected in deep oceans with high partial pressures of hydrogen (McKinnon and Zolensky 2003) and consistent with observations at Enceladus (Ray et al. 2021). Instead, sulfur is in the form of sulfide minerals (especially pyrrhotite), consistent with observations of carbonaceous chondrites (Bland et al. 2004). Sulfates start becoming a significant form of sulfur for  $\log_{10} pH_2 <$ -6. This is roughly consistent with the results from Zolotov and Kargel (2009) who found sulfate could become a significant species for  $\log_{10} pH_2 < -7$ . Furthermore, while the pH in the modeled

<sup>&</sup>lt;sup>1</sup> Potential exchange with NH<sub>4</sub><sup>+</sup> can also increase the amount of K<sup>+</sup> in solution (see section 3.2).

- compositions is consistently > 6, Tan et al. (2021) find that sulfate reduction to sulfide is favored at pH < 6.
- 285

A small fraction,  $<10^{-4}$  mol/kg of HS<sup>-</sup> and H<sub>2</sub>S are present in the three examples. As shown by Melwani Daswani et al. (2021), the potential breakdown of sulfides trapped in the rocky mantle as a consequence of thermal metamorphism may release sulfur to the ocean that may form sulfates if the conditions are sufficiently oxidizing. This potential additional contribution to salinity applies to highly evolved ocean worlds (e.g., Europa), and should be addressed in future studies.

- GWB results also show that carbon dioxide reacts with ammonia to produce organic molecules and ionic species such as acids and carboxylates, urea, and acetamide at the (few) ppm level.
- 293

Lastly, we map in a more systematic manner the salinity and EC against the concentrations of CO<sub>2</sub>

and NH<sub>3</sub>, for a reference log  $pH_2$  (bar) = 0, W/R = 10 in Figure 2. After a fraction of the CO<sub>2</sub> is

taken up in the formation of low solubility carbonate minerals such as dolomite and magnesite, high concentrations of  $HCO_3^-$  and  $CO_3^{2-}$  still remain in solution. For 0 wt.% NH<sub>3</sub>, the salinity

remains below 1 wt.% across the range of initial CO<sub>2</sub> concentration (Figure 1) and EC is <1 S/m.

Higher [NH<sub>3</sub>] in solution leads to increasing abundances of  $HCO_3^-$  and  $CO_3^2$ , relative to  $CO_2$ .

300 Relative concentrations derived from observations at Enceladus are consistent with these results

301 (Postberg et al. 2009; Glein et al. 2015). For  $[CO_2]$  in excess of 10 wt.% and  $[NH_3] = 3$  wt.%, the

302 EC exceeds 5 S/m.

303

Other dependencies of salinity and electrical conductivity were explored in this paper and are reported in the Supporting Information. The dependence on hydrostatic pressure, other lowabundance cometary volatiles, and ammonium-cation exchange is minor

307



309

Figure 3. Salinity and EC as a function of accreted CO<sub>2</sub> and NH<sub>3</sub> abundances, calculated at 0 °C, 1 atm pressure, W/R = 10, and log<sub>10</sub> pH<sub>2</sub> (bar) = 0, prior to concentration due to freezing of an ice shell. EC is

estimated following McCleskey et al. (2012). For a few cases, when  $[CO_2] > 7$  wt.%, the ionic strength of the

solution falls above the range of applicability of this method.

#### 314 **5 Conclusions and Future Applications**

- We showed that volatiles expected in objects formed from cometary materials could be major contributors to the salinity and electrical conductivity of ocean worlds. The simulations reported in this study focus on the most abundant and reactive volatile compounds expected from cometary
- composition. This yields oceans enriched in CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and NH<sub>4+</sub>, which could represent
- another endmember for the oceans of large icy moons and dwarf planets, besides chlorine- and
- 320 sulfate-based oceans (e.g., Vance et al. 2020). The amount of accreted  $NH_3$  and the water to rock
- ratio affect the solubility of carbonates. Reference abundances of  $[CO_2] = 5$  wt.% and  $[NH_3] = 0.3$
- 322 wt.% yield a salinity >2 wt.% and conductivity > 2 S/m. Accounting for higher bounds on cometary
- volatile abundances could increase the EC above 5 S/m.
- 324 Higher conductivities resulting from salt concentration with corresponding ionic strengths >1
- molal fall outside the performance space of the McCleskey et al. (2012) method. This method does
- not account for ion-ion interactions. Pawlowicz (2010) highlights a discrepancy by up to a factor
- two between the predicted EC of highly concentrated solutions for a wide range of compositions
- 328 based on theory developed for dilute solutions, and analytical measurements. Ionic interactions
- account for the bulk of that error, at least for ECs up to 10 S/m. However, EC estimates specific

to highly concentrated carbonate-rich solutions in conditions relevant to high NH<sub>4</sub>-HCO<sub>3</sub>
 concentration oceans are lacking and should be the focus of future work.

332

Sulfates were not predicted to form in any of the solutions produced in this study as sulfur was taken up by sulfides, instead. Alternative scenarios for the case of Europa could lead to the presence of sulfates in solution, either delivered from Io-genic materials and transported to the ocean via crustal overturn or other geodynamical processes to be defined. Sulfate ions may also form from the oxidation of sulfides if the ocean becomes sufficiently oxidized (Zolotov and Kargel 2009) although low pH appears to favor sulfate reduction (Tan et al. 2021).

339

Bodies likely to have accreted a large fraction of cometary volatiles include Triton and Pluto. 340 Triton could have lost a significant fraction of volatiles as a consequence of intensive heating upon 341 capture (Barr and Schwamb 2016). It is possible, however, that it had at least partially melted and 342 differentiated prior to capture. In this case, the loss of part of the hydrosphere would have resulted 343 in salt concentration. Testing the presence of a deep ocean by searching for an induced magnetic 344 field has been included in recently assessed mission concepts (e.g., at Triton, Prockter et al. 2021). 345 In Ceres, the residual brine reservoir is expected to be highly concentrated in sodium, bicarbonate, 346 ammonium, and chloride ions, in particular that make them amenable to an electromagnetic 347 sounding investigation (Grimm et al. 2021). The Uranian moons are other candidate ocean worlds. 348 These bodies are likely to be more closely related to their initial volatile compositions by being 349 less thermally processed than larger bodies, such as Ceres and Triton. Lastly, a high concentration 350 of carbonates in Titan (Brasse et al. 2017) could account for part of the high ocean density inferred 351 from the Cassini mission gravity data (Durante et al. 2019) beyond salinities predicted from rock 352 leaching only. 353

354

Estimates of salinity and EC for specific bodies need to account for evolutionary scenarios that determine the fate of volatile compounds. During differentiation of the rock from the volatile phase, some of the  $CO_2$  inventory may be sequestered in carbonates. Later on in some bodies, the release of NH<sub>3</sub> and CO<sub>2</sub> from the breakdown of organics (e.g., amino acids, insoluble organic matter), ammoniated phyllosilicates, and carbonates as a consequence of thermal metamorphism in rocky mantles (Melwani Daswani et al. 2021; Nakano et al. 2020) could increase salinity.

361

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368 acknowledged.

#### 370 **Open Research**

- 371 This research uses the Geochemist's Workbench software, version 10 <u>https://www.gwb.com/</u>
- from Aqueous Solutions LLC (Bethke, 2007). An example of input to and output from the code
- is provided in the Supporting Information file.

374

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- 536



#### Geophysical Research Letters

#### Supporting Information for

#### Contribution of Non-Water Ices to Ocean Salinity and Electrical Conductivity in Ocean Worlds

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#### **Contents of this file**

Text S1 Figures S1 to S8

#### Introduction

The supplementary information provides supporting material for some of the assumptions and conclusions presented in the main manuscript.

Figure S1 is a Bjerrum plot showing the relative predominance of nitrogen and carbon compounds as a function of pH.

Figure S2 illustrates the influence of pressure on the speciation between dissolved carbon dioxide, and carbonate and bicarbonate ions.

Figure S3 extends Figure 1's calculation of salinity for solutions rich in (bi)carbonate ions and ammonium to water to rock ratios up to 500.

Figures S4 and S5 represent the relative contributions of the main types of ions in solution for the main compositions investigated in the study.

Figure S6 illustrates the differences in salinity and electrical conductivity depending on whether magnesite and dolomite are allowed to form or are excluded from the system due to kinetic inhibition of precipitation.

Figure S7 represents the concentrations of key solutes for different water to rock ratios. It complements Figure 3.

Figure S8 illustrates the differences in salinity and electrical conductivity obtained for reference compositions and a range of log pH<sub>2</sub>.

A section entitled "Additional Dependencies of Salinity and Electrical Conductivity" reports additional analysis that revealed only minor dependencies of these two parameters on hydrostatic pressure, minor non-water ices supplied by cometary materials, and ammonium-cation exchange.

#### **1** Text S1. Approach for Supplementary Figures

2 Most of the results presented in this supplement are computed using the *React* application 3 of the *Geochemist's Workbench* (GWB) (Bethke 2007). Most figures have been obtained at 4 a default pressure of 1 atm and a temperature of 0 °C. Figure S2 illustrates the relatively 5 weak dependence of the results on pressure.

6 We use the thermo.com.V8.R6+ thermodynamic database that is largely based on the 7 database used by SUPCRT92 (Johnson et al., 1992). Access to the database can be found

8 here: <u>https://www.gwb.com/thermo.php</u>

9 That database contains the volatile compounds of interest as well as broad ranges of 10 minerals, aqueous inorganic species, and organic compounds.

11 The *Geochemist's Workbench* computes electrical conductivity using the approach by 12 McCleskey et al. (2012), which is suitable for ionic strengths up to 1 mol/kg over relevant 13 ranges of temperature (0–95 °C), pH (1–10), and conductivity (30–70,000 10<sup>-4</sup> S m<sup>-1</sup>). The 14 empirical relationships (EC as a function of temperature and ionic strength) at the basis of 15 this method were derived from conductivity measurements obtained for ~30 electrolytes 16 over a wide range of conditions. The equations were then coupled to a geochemical 17 speciation model. McCleskey et al. (2012) found that the predicted conductivity is accurate 18 to within ±5% of measurements.

19 The speciation of dissolved carbon was performed with the CHIM-XPT geochemistry 20 program, which is used to calculate simultaneous equilibrium between minerals, gases and 21 an aqueous phase under different temperature, pressure and compositions conditions, 22 using extended Debye-Hückel theory and Helgeson-Kirkham-Flowers parameters (Reed et 23 al., 1998). To monitor the effect of pressure on the speciation of dissolved carbon, we 24 titrated 1 wt. % CO<sub>2</sub> gas into 1 kg pure water at 5 kbar. We then buffered pH to 9, which is 25 consistent with the pH inferred for Enceladus' ocean (Glein and Waite, 2020). Pressure was 26 then decreased from 5 kbar to 1 bar. Because no fractionation occurs in these models, 27 Figure S2 can be read from left to right, or right to left.

- 28
- 29
- 30



33

**Figure S1.** Bjerrum plot for the key species explored in this study at 0°C and 1 atm, for initial  $[CO_2] = 1$  wt.% and  $[NH_3] = 0.3$  wt.%. 

- 38



**Figure S2.** Effect of pressure on the abundances of  $HCO_3^-$ ,  $CO_3^{2-}$ , and  $CO_2$  in solution for an initial concentration of 1 wt.%  $CO_2$  in solution and an imposed pH = 9 (consistent with estimates of the pH of Enceladus' ocean; e.g. Glein and Waite 2020) from 1 bar to 5 kbar. The fraction of  $HCO_3^-$  remains about constant while  $CO_3^{2-}$  increases by about 10 % over the full pressure range.



**Figure S3.** Dependence of salinity across water to rock ratio from 1 to 500. This figure complements Figure 1 in the main text.



Figure S4. Relative molar contributions of the main types of ions in solution for 

the main compositions investigated in this study, at log  $pH_2(bar) = 0$  and for two 

values of water to rock ratio (W/R). 





68 Figure S5. Speciation of carbon-based compounds (solids and solutes) in mol.% 69 for two reference compositions and water to rock ratios (W/R). Magnesite is 70 systematically formed in these examples. Siderite is the second dominant form of 71 solid carbonate at higher W/R, while dolomite dominates at low W/R. In solution, 72 bicarbonate dominates over the carbonate ion at high W/R, while the two are found in roughly equal proportions at low W/R. The "other" category encompasses ion 73 pairs such as NaCO<sub>3</sub><sup>-</sup>, NaHCO<sub>3</sub>(aq), MgHCO<sub>3</sub><sup>+</sup>, and MgCO<sub>3</sub>(aq). 74



**Figure S6.** Salinity and electrical conductivity estimated for a range of [CO<sub>2</sub>] and [NH<sub>3</sub>] accreted abundances assuming (left) that the formation of magnesite and dolomite is kinetically inhibited and these compounds never form, or (right) that they can form as the system reaches equilibrium. For high [CO<sub>2</sub>], the solution ionic strength can exceed the applicability region of the McCleskey et al. (2012) approach adopted in this study.



84 85

**Figure S7.** Dependence of the composition of the solutions as a function of water to rock ratio for a reference composition of 5 wt.% CO<sub>2</sub> and 0.3 wt.% NH<sub>3</sub>. This plot complements Figure 3 in the main text.



Figure S8. Differences in the salinity and EC output for a log pH<sub>2</sub> (bar) of -3 and
 of +2, relative to the -3 case.

#### 100 Additional Dependencies of Salinity and Electrical Conductivity

101

102 Other Cometary Volatiles: Additional cometary volatiles are naturally expected with CO<sub>2</sub> 103 and NH<sub>3</sub> (see Section 2), in particular CO (carbon monoxide, 1-30 wt.% of volatile fraction), 104 CH<sub>3</sub>OH (methanol, 0.4–12 wt.%),  $H_2S$  (hydrogen sulfide, 0.3–2.8 wt.%), and  $H_2CO$ 105 (formaldehyde, 0.2–2.5 wt.%), and other hydrocarbons (0.4–6 wt.%) (Mumma and Charnley 106 2011). The contribution of carbon monoxide is such that for CO abundances up to 10 wt.% 107 of the volatile fraction, the salinity and EC are both higher than the CO case by only 4 108 %. At Pluto and Triton, CO ice is found, but at much lower concentration than cometary 109 abundances (Glein and Waite, 2018). This may mean that accreted CO participated in 110 ocean chemistry and contributed to salinity, or CO was never accreted or was lost during 111 Pluto's and Triton's evolution.

Hydrocarbons are not expected to be reactive (the kinetics of reaction and redox equilibrium are slow at 0 °C). Kinetics may also depend on pH, Eh (electrical potential), and the presence of catalysts, but exploring this aspect falls beyond the scope of this study. All other volatile bases are marginal contributors of solutes based on the low abundances, a few tenths of percent, derived from astronomical observations.

117

118 Effect of Hydrostatic Pressure on Electrical Conductivity: The EC estimates presented 119 below are for a standard pressure of 0.1 MPa, and assuming that the hydrosphere is all 120 liquid, i.e., not accounting for what occurs to solute concentrations in liquids upon the 121 formation of an ice shell. In other planetary settings the predictions will differ because 122 physical conditions in the oceans can vary greatly (Vance et al. 2020). Hydrostatic pressure 123 tends to increase EC in aqueous systems, up to 200 MPa due to the increased association 124 of ions. Experiments document a change in the slope of conductivity with pressure that 125 seems to be related to the changing ion association above 200 MPa. For aqueous MgSO<sub>4</sub> 126 (low concentrations of 0.1 and 0.001 molar), Larionov and Kryukov (1984) report a negative 127 second derivative with pressure at all temperatures, and a changing first derivative from 128 positive to negative in the lower temperature range. Bannard (1975) found little 129 dependence on pressure (a few %) for a range of concentrations of NaCl from 0.01 to 1 130 mol/L, pressures up to 200 MPa, and temperatures <50 °C. At higher pressures (e.g., in 131 Titan's ocean), fluid compression reduces ionic association and the derivative of EC with 132 pressure becomes negative (Schmidt and Manning 2017, Pan et al. 2020).

133

134 NH4-Cation Exchange: Ammonium can be incorporated into the interlayers of smectite 135 clays, which thus represent a potential sink of  $NH_3$  (e.g., Engel et al. 1994) while releasing 136 K<sup>+</sup> and Na<sup>+</sup> to the ocean. Observations indicate that  $NH_4^+$  is also present in the form of 137 salts at Ceres (Raponi et al. 2019). We find that with the same concentration and all other aspects of the system being equal, K<sup>+</sup> produce a conductivity similar to  $NH_4^+$  over the pH range of interest (Figure 1). The total elemental fraction of K and Na accreted in CI-type rock is ~0.6 wt.% (or ~2.3x10<sup>-4</sup> mol per kg of rock) (e.g., Lodders 2021). That is, assuming full cation- $NH_4^+$  exchange would free up to  $2.3x10^{-4}$  mol/kg of these cations and remove that same amount of  $NH_4^+$  from the solution with negligible impact on electrical conductivity.

144

## 145 Example Input to the Geochemist's Workbench146

```
147
       [CO2] = 1 wt.%, [NH3] = 0.3%
148
149
            Temperature = 0.0 C Pressure = 1.013 bar
150
            pH = 8.827
                               \log fO2 = -80.834
151
            Eh = -0.3400 \text{ volts}
                                 pe = -6.2740
152
            lonic strength
                             = 0.207840 molal
153
            Activity of water = 0.999336
154
            Solvent mass
                                 0.89597 kg
                             =
155
            Solution mass
                                  0.91030 kg
                             =
156
            Mineral mass
                             =
                                0.093072 kg
157
            Fluid density
                            = 1.011 \text{ g/cm}3
158
             compressibility = 4.815e-05 /bar
159
              expansivity
                            = 7.894e-05 /C
160
             viscosity
                              0.018 poise
                           =
161
            Chlorinity
                           = 0.019280 molal
                                   15737 mg/kg sol'n
162
            Dissolved solids =
163
                                  18787.43 uS/cm (or umho/cm)
            Elect. conductivity =
164
            Hardness
                                1069.81 mg/kg sol'n as CaCO3
                            =
165
             carbonate
                            =
                                 1069.81 mg/kg sol'n as CaCO3
166
                                     0.00 mg/kg sol'n as CaCO3
             non-carbonate
                              =
                                   9339.63 mg/kg sol'n as CaCO3
167
            Carbonate alkalinity=
168
            Water type
                             =
                                NH4-HCO3
169
            Bulk volume
                             =
                                   931. cm3
170
            Fluid volume
                                   901. cm3
                             =
171
            Mineral volume
                              =
                                     30.3 cm3
172
            Inert volume
                                  0.000 cm3
                             =
173
            Porosity
                                 96.7 %
                           =
174
            Permeability
                                   32.1 cm2
                             =
175
            Mass reacted
                                    103 g
                             =
176
177
                      moles
                                 moles
                                            grams
                                                        cm3
                                                               rxn rate
178
        Reactants
                        remaining
                                      reacted
                                                 reacted
                                                            reacted (mol/kg sec)
179
180
        AI2O3
                       -4.144e-16
                                     0.01942
                                                  1.980
```

181	CH4(g) (fixed	fug.)	-0.07463	-1.197		
182	CO2(aq)	-3.133e-15	0.2046	9.006		
183	CaO	4.020e-16	0.02639	1.480		
184	FeO	-5.319e-15	0.3939	28.30	4.727	
185	Formaldehyd	le(aq) 9.097e	-16 0.05	999 1.8	301	
186	H2S(aq)	0.0000	0.0000	0.0000		
187	HCN(aq)	0.0000	0.0000	0.0000		
188	K2O	1.537e-17	0.0009555	0.09000	0.038	58
189	Methanol(aq	) 1.117e-1	5 0.112	4 3.602		
190	MgO	-4.481e-15	0.4660	18.78		
191	MnO	0.0000	0.0000	0.0000		
192	N2(g)	0.0000	0.0000	0.0000		
193	NH3(aq)	3.141e-15	0.1586	2.702		
194	Na2O	-1.491e-16	0.01404	0.8700	0.350	9
195	NiO	-2.571e-16	0.01982	1.480		
196	P2O5	0.0000	0.0000	0.0000		
197	S	3.319e-15	0.2195	7.040	3.405	
198	SO2(g)	0.0000	0.0000	0.0000		
199	SO4	0.0000	0.0000	0.0000		
200	SiO2	-6.491e-15	0.4464	26.82		
201						
202	Minerals in sy	stem moles	log mole	s grams	volun	ne (cm3)
203						
204	Annite	0.001300	-2.886	0.6656	0.2007	
205	Cronstedtite-	-7A 0.0426	1 -1.370	17.02	6.42	4
206	Gibbsite	0.002474	-2.607	0.1930	0.07905	
207	Huntite	0.02639	-1.579	9.317	3.244	
208	Hydromagne	site 0.0081	50 -2.089	3.811	1.7	702
209	Ni2SiO4	0.009903	-2.004	2.074	0.4220	
210	Pyrrhotite	0.2195	-0.658	19.30	3.996	
211	Saponite-Mg	0.1063	-0.974	40.69	14.20	
212		-				
213	(total)		93.07	30.27		
214			a		<i>.</i> .	
215	Aqueous spec	cies molality	/ mg/kg so	ol'n act. co	oet. log	act.
216						
217	HCO3-	0.1640	9847.	0.7353	-0.9188	
218	NH4+	0.1576	2798.	0.6974 -	-0.9590	
219	Na+	0.02561	579.6	0.7353 -	1.7251	
220	CI-	0.01921	670.4 0.	/111 -1.	8645	
221	N2(aq)	0.006583	181.5	1.0000	-2.1816	
222		0.006552	387.0	0.2935	-2./160	
223	NH3(aq)	0.006292	105.5	1.0000	-2.2012	
224	NaHCO3(aq)	0.00536	4 443.5	o 1.0000	-2.270	15

225 Mg++ 0.004591 109.8 0.3943 -2.7422 226 MgHCO3+ 0.003567 299.6 0.7353 -2.5812 227 MgCO3(aq) 0.002666 221.3 1.0000 -2.5741 228 CO2(aq) 0.0006840 29.63 1.0000 -3.1650 229 26.22 K+ 0.0006813 0.7111 -3.3147 230 NaCO3-0.0003173 25.92 0.7353 -3.6320 231 7.708e-05 4.480 0.7460 -4.2403 Acetate 232 NaCl(aq) 3.818e-05 2.196 1.0000 -4.4182 233 MqCl+ 3.002e-05 1.766 0.7353 -4.6561 234 NH4CH3COO(aq) 1.076e-05 0.8161 1.0000 -4.9683 235 0.8805 0.2935 Ni(NH3)2++ 9.645e-06 -5.5481 236 Acetamide(aq) 7.605e-06 0.4421 1.0000 -5.1189 237 Fe++ 4.835e-06 0.2658 0.3398 -5.7844 238 -5.4831 MgCH3COO+ 4.471e-06 0.3668 0.7353 239 SiO2(aq) 1.853e-06 0.1096 1.0000 -5.7321 240 0.04007 Ethane(aq) 1.354e-06 1.0000 -5.8684 241 Formate 1.081e-06 0.04790 0.7237 -6.1066 242 OH-1.065e-06 0.01782 0.7237 -6.1132 243 NaCH3COO(aq) 0.07918 -6.0085 9.806e-07 1.0000 244 Ni++ 6.516e-07 0.03764 0.3398 -6.6548 245 HS-0.009451 0.7237 2.903e-07 -6.6776 246 0.009476 1.0000 KCl(aq) 1.291e-07 -6.8889 247 Urea(aq) 1.274e-07 0.007532 1.0000 -6.8948 248 Mg(For)+ 9.058e-08 0.006180 0.7353 -7.1765 249 NaHSiO3(aq) 9.028e-08 0.008894 1.0000 -7.0444 250 HSiO3-0.006097 0.7353 -7.2286 8.035e-08 251 7.857e-08 0.005651 0.7353 -7.2383 Propanoate 252 AIO2-3.504e-08 0.002034 0.7353 -7.5889 253 FeCI+ 2.150e-08 0.001932 0.7353 -7.8012 254 1.0000 Na(For)(aq) 1.855e-08 0.001242 -7.7317 255 1.420e-08 0.001372 1.0000 -7.8476 KCH3COO(aq) 256 (only species > 1e-8 molal listed) 257 258 Mineral saturation states 259 log Q/K log Q/K 260 261 Polydymite 17.6094s/sat Dolomite-ord -0.8298 262 Heazlewoodite 11.2603s/sat Dolomite -0.8299 263 Vaesite 4.8848s/sat Greenalite -0.9758 264 -1.1002 Millerite 3.7668s/sat Quartz 265 Pyrite 3.6432s/sat Chrysotile -1.1582 266 -1.2513 С 3.3696s/sat Nesquehonite 267 Magnesite 2.1924s/sat Saponite-Ca -1.2715 268 Siderite 1.8323s/sat Talc -1.3053

269 Dawsonite 1.1677s/sat Tridymite -1.3066 270 0.6610s/sat Celadonite -1.3640 Daphnite-14A 271 Diaspore 0.4616s/sat Saponite-H -1.3718 272 Phlogopite 0.3345s/sat Chalcedony -1.3962 273 Ripidolite-14A 0.2140s/sat Artinite -1.6612 274 Troilite 0.1079s/sat Cristobalite(alp -1.7108 275 0.0134s/sat Kaolinite Boehmite -1.7246276 -1.7894 Cronstedtite-7A 0.0000 sat Chamosite-7A 277 Gibbsite 0.0000 sat Coesite -1.9798278 Hydromagnesite 0.0000 sat Nontronite-Mg -2.0718 279 Annite 0.0000 sat Maximum Microcli -2.0839 280 -2.0883 Ni2SiO4 0.0000 sat K-Feldspar 281 0.0000 sat Ferrosilite -2.1279Huntite 282 Pyrrhotite 0.0000 sat Nontronite-Na -2.1305 283 Saponite-Mg 0.0000 sat Cristobalite(bet -2.2308 Magnetite 284 -0.0005 Nontronite-K -2.2343 285 lce -0.0470 Nahcolite -2.2384 286 Saponite-Na -0.0617 Amesite-14A -2.2959 287 -2.5684 Hematite -0.1118 Minnesotaite 288 Dolomite-dis -2.5705 Saponite-K -0.1653 289 Trevorite -0.1940 SiO2(am) -2.6081290 Illite -2.8414 Goethite -0.5107 291 Clinochlore-14A -0.6176 Daphnite-7A -2.9535 292 Muscovite -0.6766 293 (only minerals with log Q/K > -3 listed) 294 295 partial 296 Gases press. (bar) fugacity fug. coef. log fug. 297 298 100.2 100.0 CH4(q)0.9976 2.0000 299 0.9995 0.7914 N2(g) 6.189 6.186 300 CO2(q)0.008592 0.008534 0.9932 -2.0689 301 0.005489 0.005026 0.9156 -2.2988 H2O(q) 302 2.695e-05 2.664e-05 0.9882 -4.5745 NH3(q)303 H2(g) 1.886e-06 1.887e-06 1.001 -5.7242 304 H2S(q)3.785e-08 3.747e-08 0.9900 -7.4263 305 CO(q)5.705e-12 5.705e-12 1.000\* -11.2438 306 C2H4(g) 3.240e-18 3.240e-18 1.000\* -17.4894 307 6.807e-19 6.807e-19 1.000\* -18.1671 HCI(q)308 SO2(q)4.102e-32 4.014e-32 0.9786 -31.3964 309 1.695e-32 1.695e-32 1.000\* -31.7707 S2(g) 310 NO(q) 3.974e-57 3.974e-57 1.000\* -56.4008 311 1.965e-61 1.965e-61 1.000\* -60.7066 Na(g) 312 K(g) 1.253e-63 1.253e-63 1.000\* -62.9019

1.000\* -66.9541 313 Cl2(g) 1.111e-67 1.111e-67 314 O2(q) 1.467e-81 1.465e-81 0.9990 -80.8341 315 NO2(q) 4.077e-90 4.077e-90 1.000\* -89.3897 316 1.307e-100 1.307e-100 1.000\* -99.8838 Mg(g) 317 C(q) 1.916e-126 1.916e-126 1.000\* -125.7175 318 1.000\* -132.1960 Ca(g) 6.369e-133 6.369e-133 319 5.955e-150 5.955e-150 1.000\* -149.2251 Al(g) 320 Si(q) 7.427e-164 7.427e-164 1.000\* -163.1292 321 \*no data, gas taken to be ideal 322 323 In fluid Sorbed 324 Original basis total moles moles mg/kg moles mg/kg 325 \_\_\_\_\_ 326 H2O 50.6 49.7 9.84e+05 327 Al+++ 0.0388 3.19e-08 0.000945 328 Ca++ 0.0264 2.15e-10 9.46e-06 329 Cl-0.0173 0.0173 673. 330 Fe++ 0.394 4.35e-06 0.267 331 H+ -1.20 0.133 148. 332 HCO3-0.302 0.164 1.10e+04 333 HPO4--9.38e-12 9.38e-12 9.89e-07 334 K+ 0.00191 0.000611 26.2 335 Mg++ 0.466 0.00973 260. 336 Mn++ 1.64e-11 1.64e-11 9.89e-07 337 NH3(aq) 0.159 0.159 2.97e+03 338 Na+ 0.0281 0.0281 709. 339 Ni++ 0.0198 9.23e-06 0.595 340 O2(aq) -0.409 0.00866 304. 341 0.220 2.67e-07 0.0282 SO4--342 0.446 1.81e-06 0.120 SiO2(aq) 343 344 Elemental composition In fluid Sorbed 345 total moles moles mg/kg moles mg/kg 346 \_\_\_\_\_ 347 Aluminum 0.03884 3.188e-08 0.0009448 348 Calcium 0.02639 2.148e-10 9.455e-06 349 Carbon 0.3024 0.1643 2167. 350 Chlorine 0.01727 0.01727 672.8 351 Hydrogen 100.7 100.2 1.109e+05 352 0.3939 4.355e-06 Iron 0.2672 353 Magnesium 0.4660 0.009730 259.8 354 Manganese 1.639e-11 1.639e-11 9.894e-07 355 Nickel 0.01982 9.227e-06 0.5949 356 Nitrogen 0.1586 0.1586 2441.

357	Oxygen	52.41	50.23 8	.828e+05
358	Phosphorus	9.383e-12	9.383e-	12 3.193e-07
359	Potassium	0.001911	0.000610	26.22
360	Silicon	0.4464 1.8	13e-06	0.05595
361	Sodium	0.02807	0.02807	709.0
362	Sulfur	0.2195 2.6	74e-07	0.009420