

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

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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 $p\text{H}_2$.

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.

Text S1. Approach for Supplementary Figures

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

We use the thermo.com.V8.R6+ thermodynamic database that is largely based on the database used by SUPCRT92 (Johnson et al., 1992). Access to the database can be found here: <https://www.gwb.com/thermo.php>

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

The *Geochemist's Workbench* computes electrical conductivity using the approach by McCleskey et al. (2012), which is suitable for ionic strengths up to 1 mol/kg over relevant ranges of temperature (0–95 °C), pH (1–10), and conductivity (30–70,000 10^{-4} S m^{-1}). The empirical relationships (EC as a function of temperature and ionic strength) at the basis of this method were derived from conductivity measurements 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 accurate to within $\pm 5\%$ of measurements.

The speciation of dissolved carbon was performed with the CHIM-XPT geochemistry program, which is used to calculate simultaneous equilibrium between minerals, gases and an aqueous phase under different temperature, pressure and compositions conditions, using extended Debye-Hückel theory and Helgeson-Kirkham-Flowers parameters (Reed et al., 1998). To monitor the effect of pressure on the speciation of dissolved carbon, we titrated 1 wt. % CO₂ gas into 1 kg pure water at 5 kbar. We then buffered pH to 9, which is consistent with the pH inferred for Enceladus' ocean (Glein and Waite, 2020). Pressure was then decreased from 5 kbar to 1 bar. Because no fractionation occurs in these models, Figure S2 can be read from left to right, or right to left.

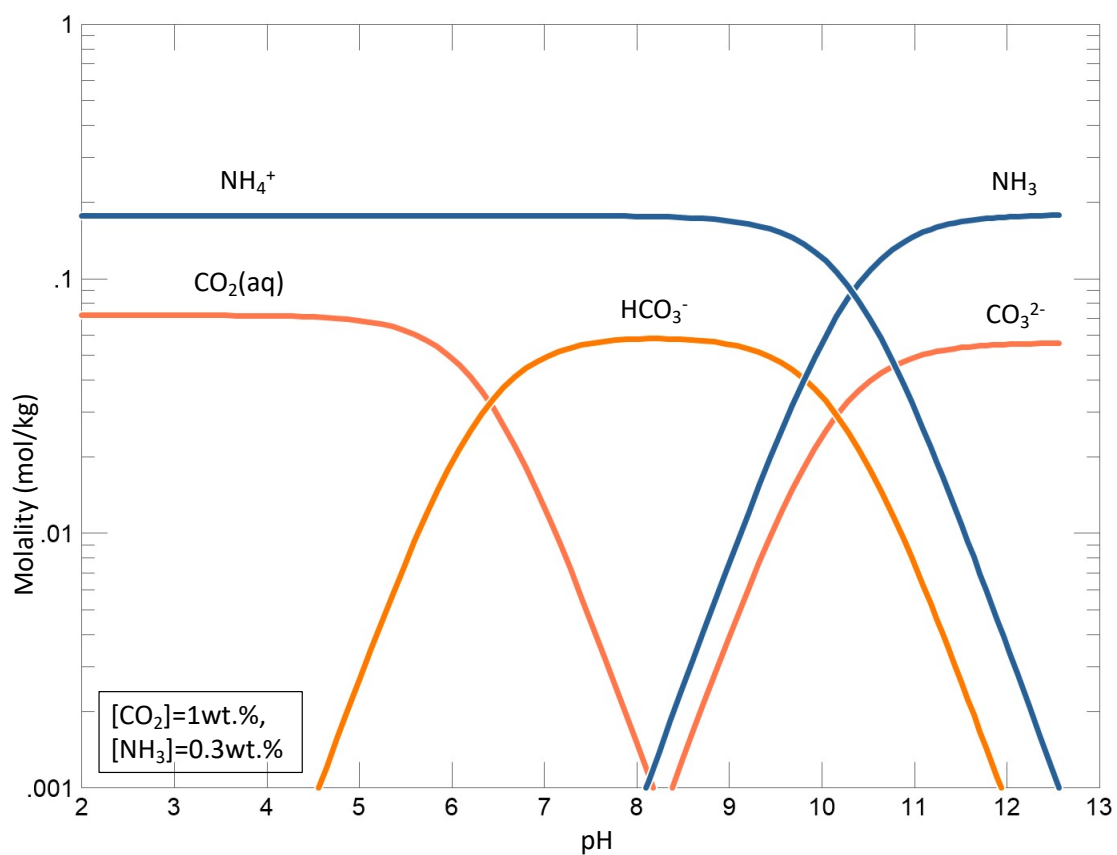


Figure S1. Bjerrum plot for the key species explored in this study at 0°C and 1 atm, for initial $[\text{CO}_2] = 1 \text{ wt.}\%$ and $[\text{NH}_3] = 0.3 \text{ wt.}\%$.

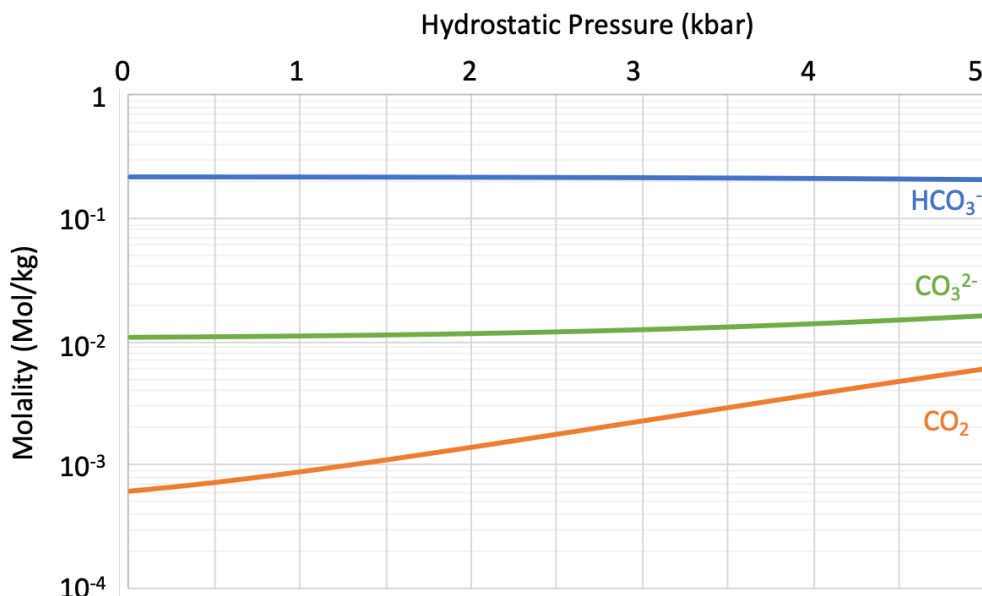


Figure S2. Effect of pressure on the abundances of HCO_3^- , CO_3^{2-} , and CO_2 in solution for an initial concentration of 1 wt.% CO_2 in solution and an imposed pH = 9 (consistent with estimates of the pH of Enceladus' ocean; e.g. Glein and Waite 2020) from 1 bar to 5 kbar. The fraction of HCO_3^-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

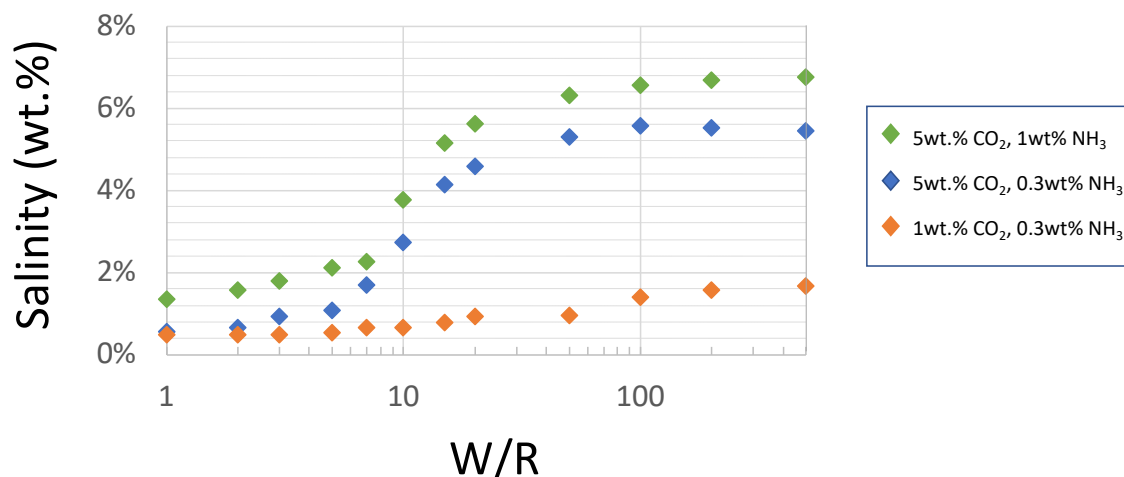
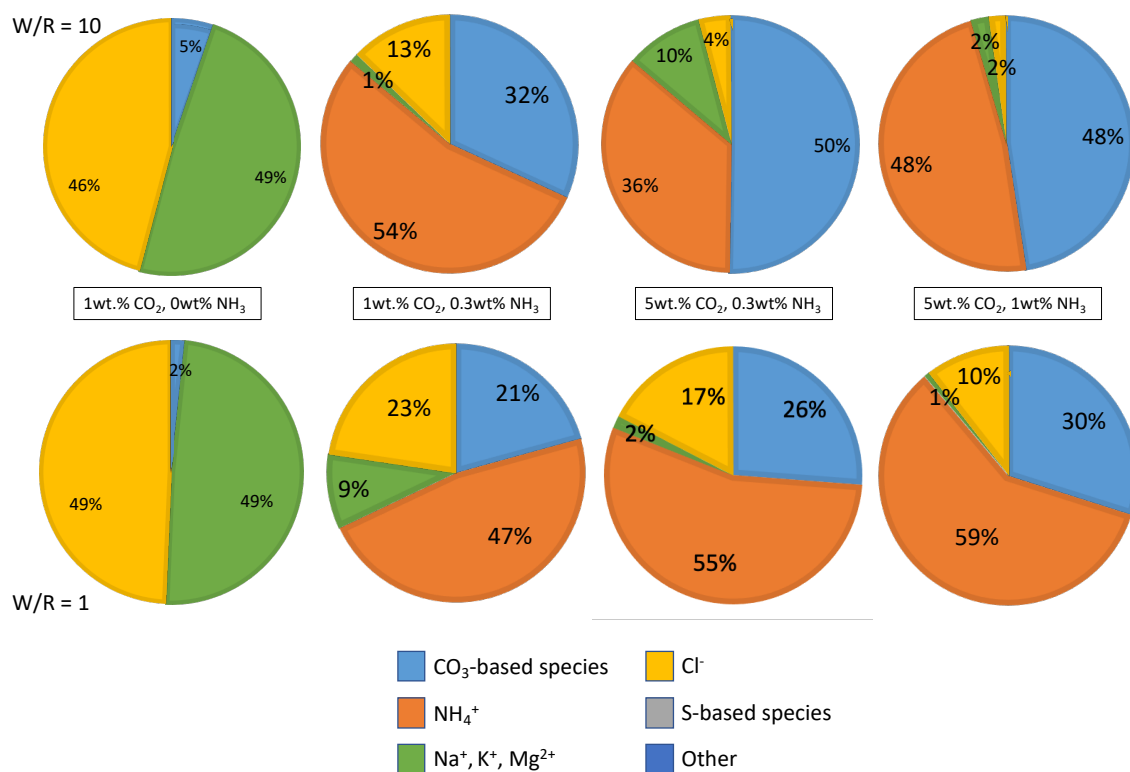


Figure S3. Dependence of salinity across water to rock ratio from 1 to 500. This figure complements Figure 1 in the main text.

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Figure S4. Relative molar contributions of the main types of ions in solution for the main compositions investigated in this study, at $\log p_{H_2}(\text{bar}) = 0$ and for two values of water to rock ratio (W/R).

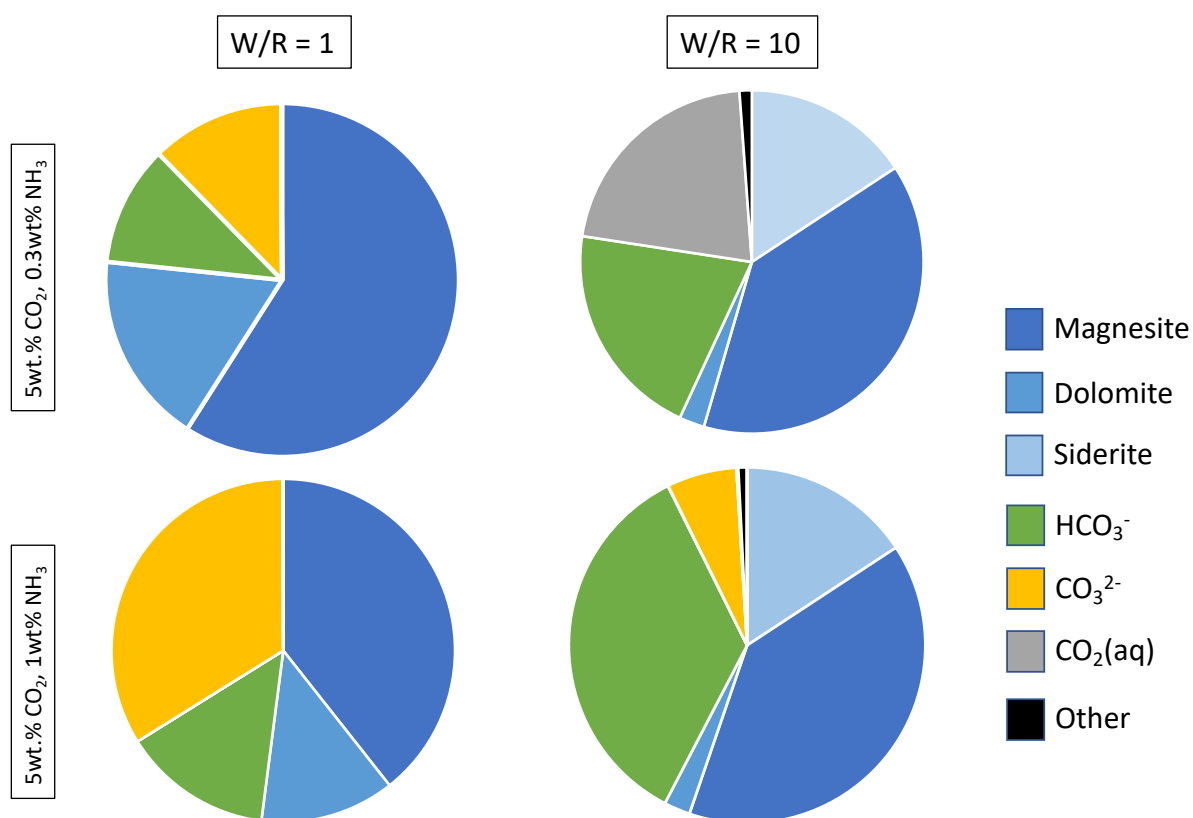


Figure S5. Speciation of carbon-based compounds (solids and solutes) in mol.% for two reference compositions and water to rock ratios (W/R). Magnesite is systematically formed in these examples. Siderite is the second dominant form of solid carbonate at higher W/R, while dolomite dominates at low W/R. In solution, 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 pairs such as NaCO₃⁻, NaHCO₃(aq), MgHCO₃⁺, and MgCO₃(aq).

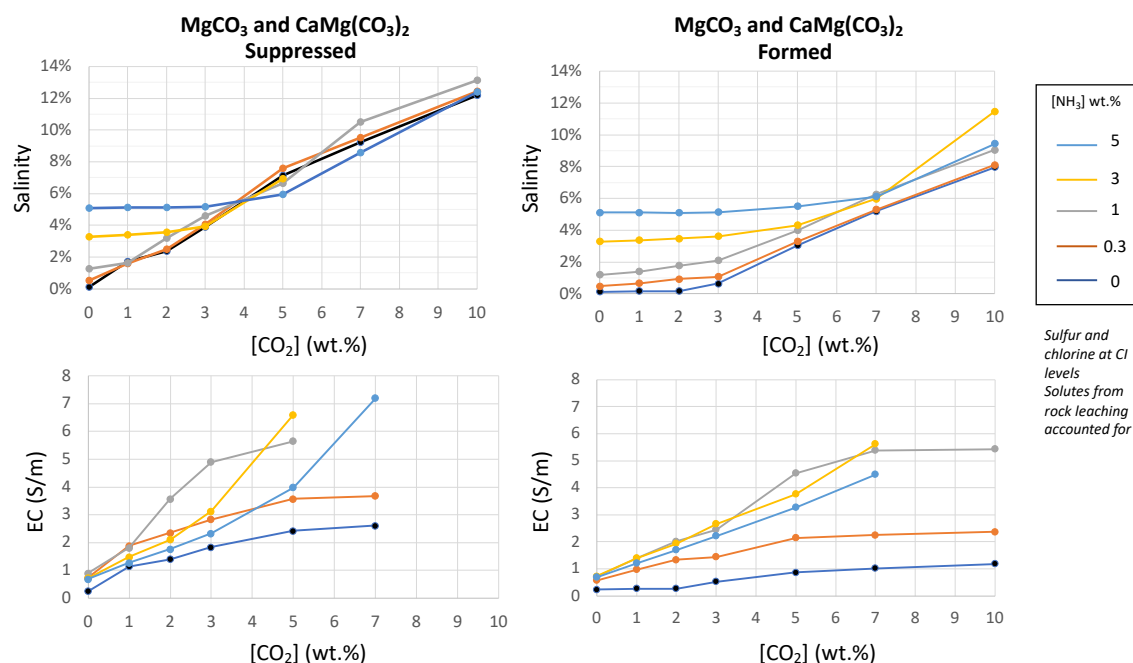


Figure S6. Salinity and electrical conductivity estimated for a range of [CO₂] and [NH₃] accreted abundances assuming (left) that the formation of magnesite and dolomite is kinetically inhibited and these compounds never form, or (right) that they can form as the system reaches equilibrium. For high [CO₂], the solution ionic strength can exceed the applicability region of the McCleskey et al. (2012) approach adopted in this study.

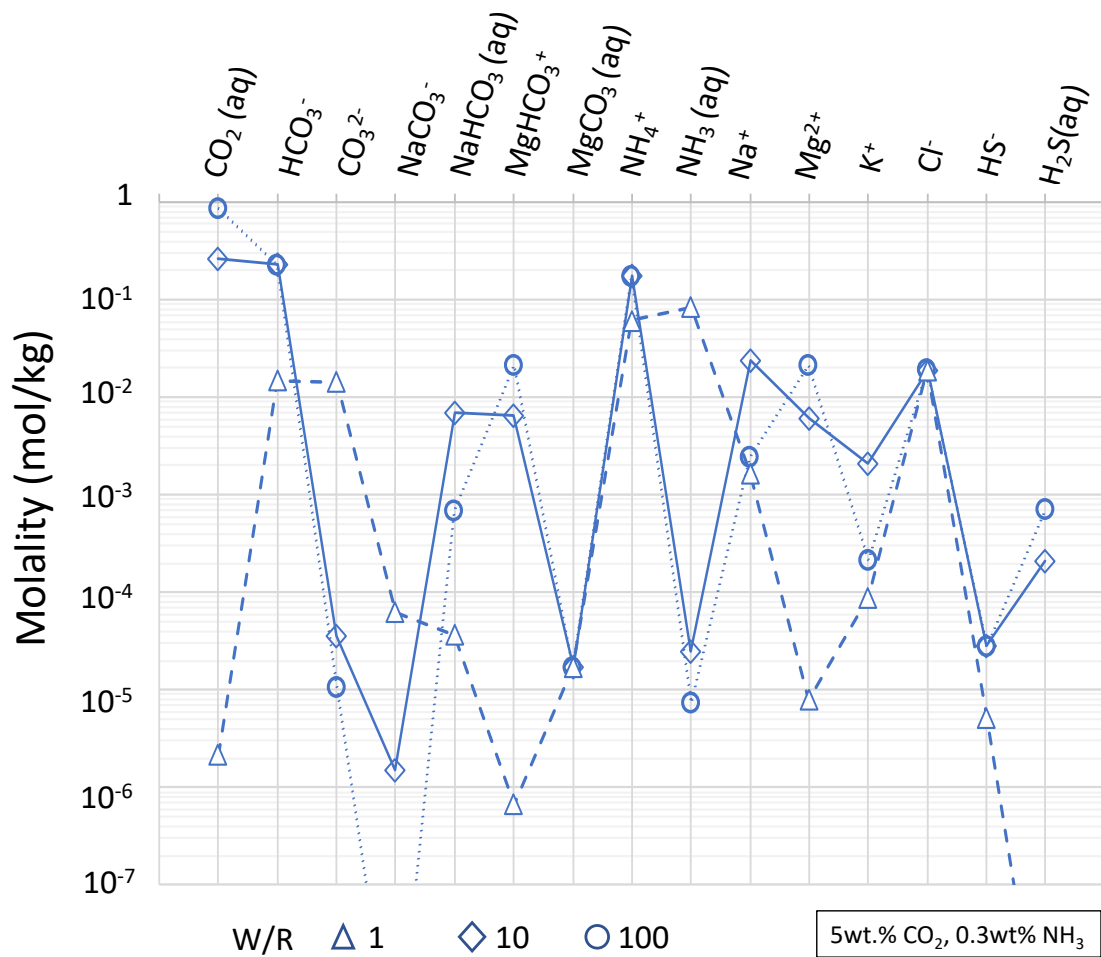
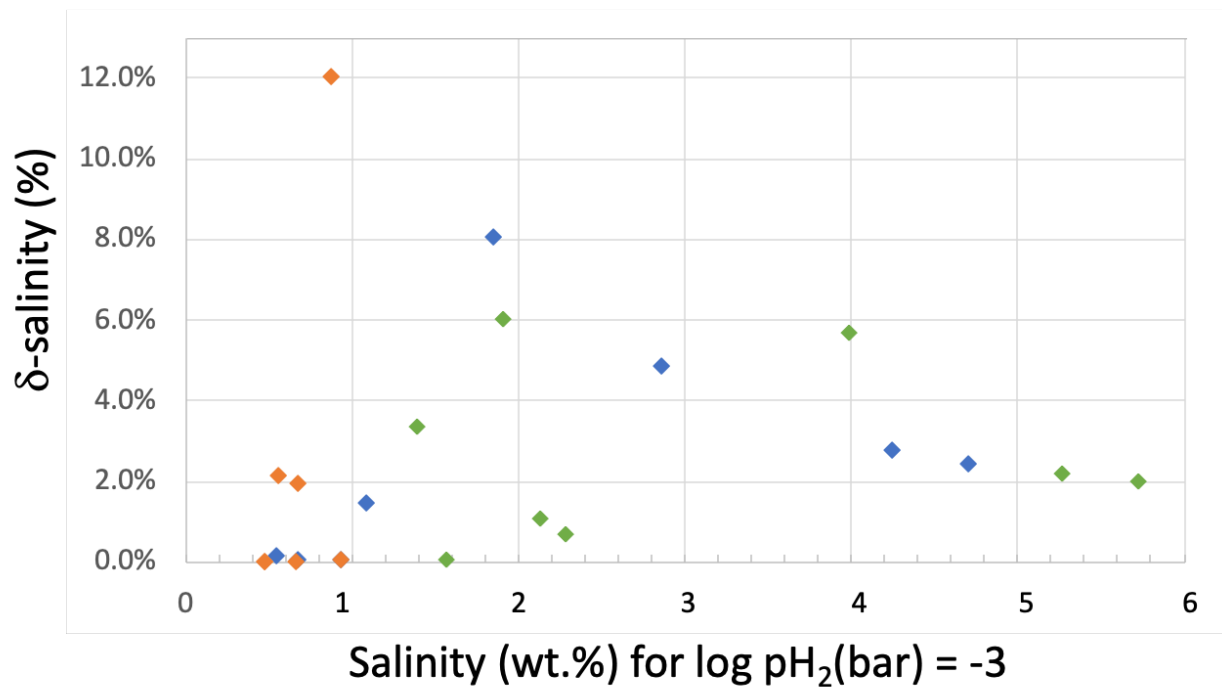
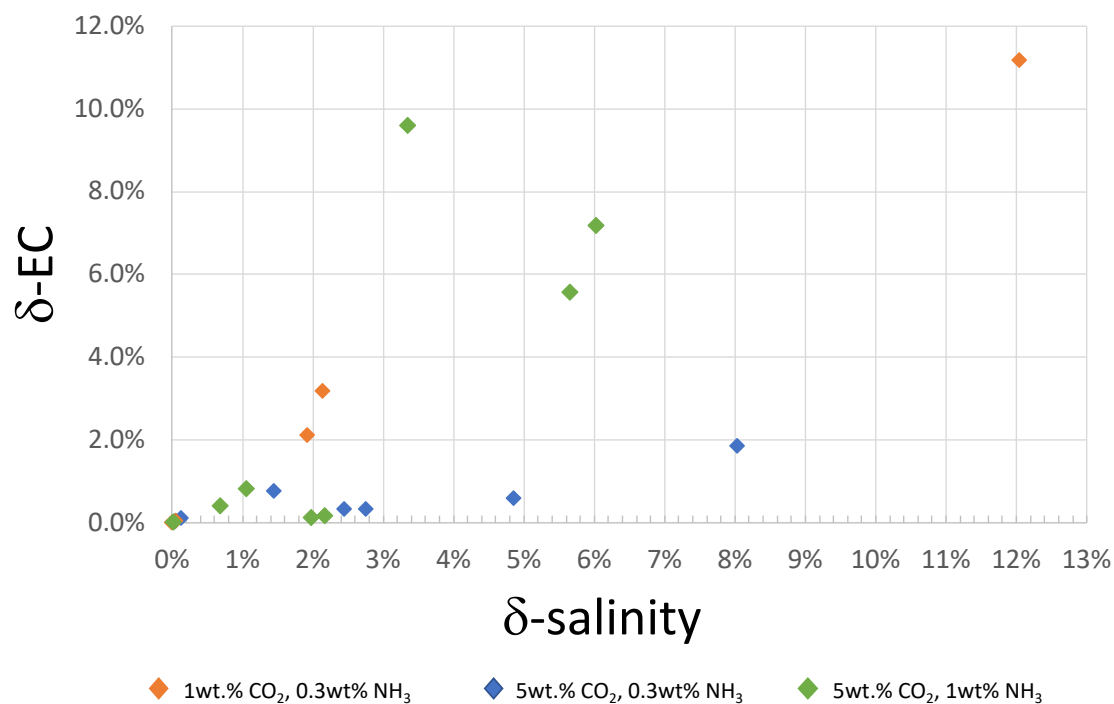


Figure S7. Dependence of the composition of the solutions as a function of water to rock ratio for a reference composition of 5 wt.% CO_2 and 0.3 wt.% NH_3 . This plot complements Figure 3 in the main text.

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Figure S8. Differences in the salinity and EC output for a log pH₂ (bar) of -3 and of +2, relative to the -3 case.

Additional Dependencies of Salinity and Electrical Conductivity

Other Cometary Volatiles: Additional cometary volatiles are naturally expected with CO₂ and NH₃ (see Section 2), in particular CO (carbon monoxide, 1–30 wt.% of volatile fraction), CH₃OH (methanol, 0.4–12 wt.%), H₂S (hydrogen sulfide, 0.3–2.8 wt.%), and H₂CO (formaldehyde, 0.2–2.5 wt.%), and other hydrocarbons (0.4–6 wt.%) (Mumma and Charnley 2011). The contribution of carbon monoxide is such that for CO abundances up to 10 wt.% of the volatile fraction, the salinity and EC are both higher than the CO case by only 4 %. At Pluto and Triton, CO ice is found, but at much lower concentration than cometary abundances (Glein and Waite, 2018). This may mean that accreted CO participated in ocean chemistry and contributed to salinity, or CO was never accreted or was lost during 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.

Effect of Hydrostatic Pressure on Electrical Conductivity: The EC estimates presented below are for a standard pressure of 0.1 MPa, and assuming that the hydrosphere is all liquid, i.e., not accounting for what occurs to solute concentrations in liquids upon the formation of an ice shell. In other planetary settings the predictions will differ because physical conditions in the oceans can vary greatly (Vance et al. 2020). Hydrostatic pressure tends to increase EC in aqueous systems, up to 200 MPa due to the increased association of ions. Experiments document a change in the slope of conductivity with pressure that seems to be related to the changing ion association above 200 MPa. For aqueous MgSO₄ (low concentrations of 0.1 and 0.001 molar), Larionov and Kryukov (1984) report a negative second derivative with pressure at all temperatures, and a changing first derivative from positive to negative in the lower temperature range. Bannard (1975) found little dependence on pressure (a few %) for a range of concentrations of NaCl from 0.01 to 1 mol/L, pressures up to 200 MPa, and temperatures <50 °C. At higher pressures (e.g., in Titan's ocean), fluid compression reduces ionic association and the derivative of EC with pressure becomes negative (Schmidt and Manning 2017, Pan et al. 2020).

NH₄-Cation Exchange: Ammonium can be incorporated into the interlayers of smectite clays, which thus represent a potential sink of NH₃ (e.g., Engel et al. 1994) while releasing K⁺ and Na⁺ to the ocean. Observations indicate that NH₄⁺ is also present in the form of salts at Ceres (Raponi et al. 2019). We find that with the same concentration and all other

aspects of the system being equal, K^+ 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 $\sim 2.3 \times 10^{-4}$ mol per kg of rock) (e.g., Lodders 2021). That is, assuming full cation- NH_4^+ exchange would free up to 2.3×10^{-4} mol/kg of these cations and remove that same amount of NH_4^+ from the solution with negligible impact on electrical conductivity.

Example Input to the Geochemist's Workbench

[CO₂] = 1 wt.%, [NH₃] = 0.3%

Temperature = 0.0 C Pressure = 1.013 bar
 pH = 8.827 log fO₂ = -80.834
 Eh = -0.3400 volts pe = -6.2740
 Ionic strength = 0.207840 molal
 Activity of water = 0.999336
 Solvent mass = 0.89597 kg
 Solution mass = 0.91030 kg
 Mineral mass = 0.093072 kg
 Fluid density = 1.011 g/cm³
 compressibility = 4.815e-05 /bar
 expansivity = 7.894e-05 /C
 viscosity = 0.018 poise
 Chlorinity = 0.019280 molal
 Dissolved solids = 15737 mg/kg sol'n
 Elect. conductivity = 18787.43 uS/cm (or umho/cm)
 Hardness = 1069.81 mg/kg sol'n as CaCO₃
 carbonate = 1069.81 mg/kg sol'n as CaCO₃
 non-carbonate = 0.00 mg/kg sol'n as CaCO₃
 Carbonate alkalinity = 9339.63 mg/kg sol'n as CaCO₃
 Water type = NH₄-HCO₃
 Bulk volume = 931. cm³
 Fluid volume = 901. cm³
 Mineral volume = 30.3 cm³
 Inert volume = 0.000 cm³
 Porosity = 96.7 %
 Permeability = 32.1 cm²
 Mass reacted = 103 g

	moles	moles	grams	cm ³	rxn rate
Reactants	remaining	reacted	reacted	reacted	(mol/kg sec)
-----	-----	-----	-----	-----	-----
Al ₂ O ₃	-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	Formaldehyde(aq)	9.097e-16	0.05999	1.801	--
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	0.03858
189	Methanol(aq)	1.117e-15	0.1124	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	0.3509
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 system	moles	log moles	grams	volume (cm3)
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203

204	Annite	0.001300	-2.886	0.6656	0.2007
205	Cronstedtite-7A	0.04261	-1.370	17.02	6.424
206	Gibbsite	0.002474	-2.607	0.1930	0.07905
207	Huntite	0.02639	-1.579	9.317	3.244
208	Hydromagnesite	0.008150	-2.089	3.811	1.702
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	
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214

215	Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
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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	Cl-	0.01921	670.4	0.7111	-1.8645
221	N2(aq)	0.006583	181.5	1.0000	-2.1816
222	CO3--	0.006552	387.0	0.2935	-2.7160
223	NH3(aq)	0.006292	105.5	1.0000	-2.2012
224	NaHCO3(aq)	0.005364	443.5	1.0000	-2.2705

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	K+	0.0006813	26.22	0.7111	-3.3147
230	NaCO3-	0.0003173	25.92	0.7353	-3.6320
231	Acetate	7.708e-05	4.480	0.7460	-4.2403
232	NaCl(aq)	3.818e-05	2.196	1.0000	-4.4182
233	MgCl+	3.002e-05	1.766	0.7353	-4.6561
234	NH4CH3COO(aq)	1.076e-05	0.8161	1.0000	-4.9683
235	Ni(NH3)2++	9.645e-06	0.8805	0.2935	-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	MgCH3COO+	4.471e-06	0.3668	0.7353	-5.4831
239	SiO2(aq)	1.853e-06	0.1096	1.0000	-5.7321
240	Ethane(aq)	1.354e-06	0.04007	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)	9.806e-07	0.07918	1.0000	-6.0085
244	Ni++	6.516e-07	0.03764	0.3398	-6.6548
245	HS-	2.903e-07	0.009451	0.7237	-6.6776
246	KCl(aq)	1.291e-07	0.009476	1.0000	-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-	8.035e-08	0.006097	0.7353	-7.2286
251	Propanoate	7.857e-08	0.005651	0.7353	-7.2383
252	AlO2-	3.504e-08	0.002034	0.7353	-7.5889
253	FeCl+	2.150e-08	0.001932	0.7353	-7.8012
254	Na(For)(aq)	1.855e-08	0.001242	1.0000	-7.7317
255	KCH3COO(aq)	1.420e-08	0.001372	1.0000	-7.8476
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	Millerite	3.7668s/sat	Quartz	-1.1002
265	Pyrite	3.6432s/sat	Chrysotile	-1.1582
266	C	3.3696s/sat	Nesquehonite	-1.2513
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	Daphnite-14A	0.6610s/sat	Celadonite	-1.3640
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	Boehmite	0.0134s/sat	Kaolinite	-1.7246
276	Cronstedtite-7A	0.0000 sat	Chamosite-7A	-1.7894
277	Gibbsite	0.0000 sat	Coesite	-1.9798
278	Hydromagnesite	0.0000 sat	Nontronite-Mg	-2.0718
279	Annite	0.0000 sat	Maximum_Microcli	-2.0839
280	Ni2SiO4	0.0000 sat	K-Feldspar	-2.0883
281	Huntite	0.0000 sat	Ferrosilite	-2.1279
282	Pyrrhotite	0.0000 sat	Nontronite-Na	-2.1305
283	Saponite-Mg	0.0000 sat	Cristobalite(bet)	-2.2308
284	Magnetite	-0.0005	Nontronite-K	-2.2343
285	Ice	-0.0470	Nahcolite	-2.2384
286	Saponite-Na	-0.0617	Amesite-14A	-2.2959
287	Hematite	-0.1118	Minnesotaite	-2.5684
288	Saponite-K	-0.1653	Dolomite-dis	-2.5705
289	Trevorite	-0.1940	SiO2(am)	-2.6081
290	Goethite	-0.5107	Illite	-2.8414
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	CH4(g)	100.2	100.0	0.9976	2.0000
299	N2(g)	6.189	6.186	0.9995	0.7914
300	CO2(g)	0.008592	0.008534	0.9932	-2.0689
301	H2O(g)	0.005489	0.005026	0.9156	-2.2988
302	NH3(g)	2.695e-05	2.664e-05	0.9882	-4.5745
303	H2(g)	1.886e-06	1.887e-06	1.001	-5.7242
304	H2S(g)	3.785e-08	3.747e-08	0.9900	-7.4263
305	CO(g)	5.705e-12	5.705e-12	1.000*	-11.2438
306	C2H4(g)	3.240e-18	3.240e-18	1.000*	-17.4894
307	HCl(g)	6.807e-19	6.807e-19	1.000*	-18.1671
308	SO2(g)	4.102e-32	4.014e-32	0.9786	-31.3964
309	S2(g)	1.695e-32	1.695e-32	1.000*	-31.7707
310	NO(g)	3.974e-57	3.974e-57	1.000*	-56.4008
311	Na(g)	1.965e-61	1.965e-61	1.000*	-60.7066
312	K(g)	1.253e-63	1.253e-63	1.000*	-62.9019

313	Cl ₂ (g)	1.111e-67	1.111e-67	1.000*	-66.9541
314	O ₂ (g)	1.467e-81	1.465e-81	0.9990	-80.8341
315	NO ₂ (g)	4.077e-90	4.077e-90	1.000*	-89.3897
316	Mg(g)	1.307e-100	1.307e-100	1.000*	-99.8838
317	C(g)	1.916e-126	1.916e-126	1.000*	-125.7175
318	Ca(g)	6.369e-133	6.369e-133	1.000*	-132.1960
319	Al(g)	5.955e-150	5.955e-150	1.000*	-149.2251
320	Si(g)	7.427e-164	7.427e-164	1.000*	-163.1292

*no data, gas taken to be ideal

		In fluid		Sorbed	
	Original basis	total moles	moles	mg/kg	moles mg/kg
326	H ₂ O	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	HCO ₃ -	0.302	0.164	1.10e+04	
333	HPO ₄ --	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	NH ₃ (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	O ₂ (aq)	-0.409	0.00866	304.	
341	SO ₄ --	0.220	2.67e-07	0.0282	
342	SiO ₂ (aq)	0.446	1.81e-06	0.120	

	Elemental composition	In fluid		Sorbed	
	total moles	moles	mg/kg	moles	mg/kg
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	Iron	0.3939	4.355e-06	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	0.0006105	26.22
360	Silicon	0.4464	1.813e-06	0.05595
361	Sodium	0.02807	0.02807	709.0
362	Sulfur	0.2195	2.674e-07	0.009420