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Abundant phosphorus expected for possible life in Enceladus's ocean

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Saturn's moon Enceladus has a potentially habitable subsurface water ocean that contains canonical building blocks of life (organic and inorganic carbon, ammonia, possibly hydrogen sulfide) and chemical energy (disequilibria for methanogenesis). However, its habitability could be strongly affected by the unknown availability of phosphorus (P). Here, we perform thermodynamic and kinetic modeling that simulates P geochemistry based on recent insights into the geochemistry of the ocean–seafloor system on Enceladus. We find that aqueous P should predominantly exist as orthophosphate (e.g., HPO_4^{2-}), and total dissolved inorganic P could reach 10^{-7} to 10^{-2} mol/kg H_2O, generally increasing with lower pH and higher dissolved CO_2, but also depending upon dissolved ammonia and silica. Levels are much higher than $<10^{-10}$ mol/kg H_2O from previous estimates and close to or higher than $\sim 10^{-6}$ mol/kg H_2O in modern Earth seawater. The high P concentration is primarily ascribed to a high (bi)carbonate concentration, which decreases the concentrations of multivalent cations via carbonate mineral formation, allowing phosphate to accumulate. Kinetic modeling of phosphate mineral dissolution suggests that geologically rapid release of P from seafloor weathering of a chondritic rocky core could supply millimoles of total dissolved P per kilogram of H_2O within 10^5 y, much less than the likely age of Enceladus's ocean (10^8 to 10^9 y). These results provide further evidence of habitable ocean conditions and show that any oceanic life would not be inhibited by low P availability.

Enceladus ocean | habitability | phosphorus | water–rock interaction | carbonates

The search for habitable worlds is usually guided by the presence of liquid water. Apart from Earth, water oceans also exist in the subsurface regions of some icy bodies (e.g., Enceladus, Europa, and Titan) in the outer solar system. The evidence for an ocean is strongest at Enceladus, where a water-rich plume erupts from a subsurface ocean (1, 2). Moreover, habitability is determined by other environmental factors, such as the availability of energy and CHNOPS elements (3). Data from the Cassini spacecraft indicate that Enceladus's ocean likely satisfies most of these other requirements for life. For example, the abundance of molecular hydrogen that coexists with CO_2 in the plume suggests the availability of chemical energy that could support methanogens (4–6). Carbon dioxide and a variety of organic compounds, which can serve as carbon sources for microorganisms, are also abundant in the plume (4, 7–9). Detected ammonia (4) or organic amines (8), and tentatively detected hydrogen sulfide (9, 10), could provide biologically useable nitrogen and sulfur, respectively.

However, a notable ingredient for habitability that has eluded detection on Enceladus is phosphorus. In terrestrial life, phosphorus in the form of orthophosphate (PO_4^{3-} and its conjugate acids) participates in biological and prebiological reactions. For example, it forms kinetically stable, charged linkages in genetic molecules and phospholipids and is used to transfer metabolic energy primarily via adenosine triphosphate (11). Phosphorus is essential and its availability is often a limiting factor for biological productivity (12, 13). Because phosphate is yet to be detected in the Enceladus plume or in Saturn's E Ring (14, 15), geochemical modeling is necessary to constrain the availability of this critical nutrient in Enceladus's ocean. Existing models (16–18) predict a very low concentration of phosphate [$<10^{-10}$ mol/kg H_2O or molal, vs. $\sim 10^{-6}$ molal in Earth's oceans (19)], which challenges the current perception of Enceladus's ocean as a habitable environment. However, those models are not based on the latest understanding of the geochemistry of the ocean–seafloor system on Enceladus (20–22). In addition to phosphate, reduced forms of phosphorus could be present and might support prebiotic chemistry. Examples include phosphine (PH_3) acquired from the solar nebula (23) or phosphite (HPO_3^{2-} and its conjugate acids) formed from aqueous alteration of accreted chondritic rocks (24). Neither of these forms of phosphorus have been identified at Enceladus (10), and it is unknown how stable these species would be in its ocean.

Significance

Enceladus is one of the prime targets in the search for life in the solar system. Observations made by the Cassini spacecraft show that this small moon of Saturn has an ice-covered water ocean that erupts into space, forming a plume that contains almost all of the basic requirements of terrestrial life. However, the bioessential element phosphorus has yet to be found. Here, we perform geochemical modeling, constrained by Cassini data, to predict how much phosphorus could be present in the Enceladus ocean. These models suggest that Enceladus's ocean should be relatively rich in dissolved phosphorus. This means that there can now be greater confidence that the ocean of Enceladus is habitable.

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Here, we present thermodynamic and kinetic modeling results on the chemical speciation and solubility of phosphorus in Enceladus ocean water. Our results suggest the predominant stability of orthophosphate (vs. instability of reduced forms of P) and relatively high solubility in alkaline and carbonate-rich water.

Results and Discussion

We begin by evaluating the thermodynamic stabilities of different forms of dissolved phosphorus on Enceladus. Fig. 1 shows the predominance regions of P species as a function of pH and equilibrium oxidation state at 0 °C. The redox state is represented by the activity of H_2, which is approximately equal to the molal concentration of H_2 in solutions that are not brines. The Enceladus ocean is thought to be relatively reducing because H_2 is abundant in the plume gas (4, 21). Nevertheless, oxidized P (in the form of phosphates) is likely to be the most stable form of phosphorus in the ocean, as presently constrained activities of H_2 are insufficient to favor reduced forms of P (including +III and −III oxidation states) at equilibrium (Fig. 1). Even in the most extreme scenario, where the H_2 activity is maximized by assuming that the H_2 fugacity is similar to the seafloor pressure [~70 bars (21)], oxidized P(+V) should be the most stable form of P. Only low-level concentrations of reduced P species can be maintained outside of their predominance regions (*SI Appendix*, Fig. S1). Higher concentrations of metastable reduced P species might occur if they were delivered recently to the ocean from an exogenous source [e.g., a cometary impact (25)] or from iron phosphide corrosion deep in the rocky core (24). We regard the persistence of significantly unstable P species from the early history of Enceladus as unlikely if the ocean is relatively long-lived ($\gtrsim$100 My) (26–28) and hydrothermally processed (4, 22, 29). Assuming that thermodynamic stability is the chief determinant, then orthophosphate would be the most abundant form of P in the ocean of Enceladus.

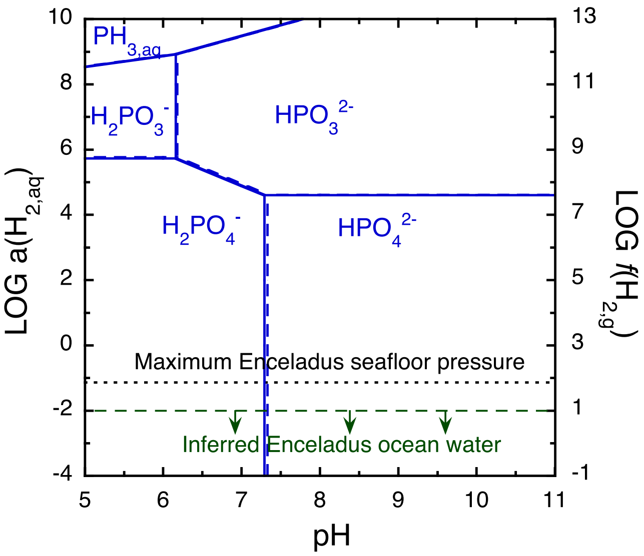

Fig. 1. Thermodynamically favored form of dissolved phosphorus as a function of pH and equilibrium oxidation state (as activity of dissolved hydrogen, or fugacity of hydrogen gas in bars) at 0 °C and 70 bars (1 bar for reference in dashed lines). Within its predominance region, the indicated species would have the highest activity out of all aqueous P species if equilibrium is reached. The observationally based upper limit on $a(H_{2,aq})$ (dashed green line) is from Waite et al. (4), and the theoretical upper limit on $f(H_{2,g})$ (dotted black line) is from Glein et al. (21). Diphosphate species do not appear in this plot since they constitute less than ~0.1% of the equilibrium P budget for total P concentrations up to 100 mmolal (*SI Appendix*, Fig. S13).

The next question is how much orthophosphate could be in the ocean? By mass balance, complete leaching of a chondritic inventory of phosphorus from Enceladus's core into its ocean would result in up to ~100 mmolal dissolved P (*SI Appendix*, Table S6). If interplanetary dust particles are more compositionally analogous to the rock component in the building blocks of Enceladus (which are unknown), then a modestly larger P inventory may be implied (30). However, total dissolution represents an upper limit, and more realistic estimates can be made by calculating the solubilities of phosphate minerals under Enceladus ocean conditions. The solubilities are constrained by the thermodynamic properties of minerals and aqueous species, and the conditions are constrained by Cassini observations (*Methods* and *SI Appendix*, section S1 and Table S2). The ocean pH is treated as the primary independent variable with a range, since there is some disagreement between published values (21). Application of the above constraints leads to predictions of the orthophosphate concentration (mainly as HPO_4^{2-}) at equilibrium. We find that its concentration can reach up to several millimolal over a range of previously proposed pH values from 8.5 to 11 (14, 20, 22, 31, 32) (Fig. 2 and *SI Appendix*, Fig. S2). This relatively high level of dissolved P persists under a much broader range of environmental conditions (*SI Appendix*, section S3).

Phosphorus concentration also depends on the amounts of inorganic carbon and ammonia (Fig. 2 and *SI Appendix*, Figs. S2, S4, S5, and S8). When inorganic carbon is abundant, it keeps divalent cations (Ca, Mg, Fe, etc.) in carbonate minerals (e.g., calcite, magnesite, dolomite, and siderite; *SI Appendix*, Fig. S3), which promotes leaching of P from phosphate minerals so that Enceladus ocean water can reach a state of saturation with respect to the most stable phosphate mineral. In addition, phosphorus concentration is found to be inversely related to the concentration of total ammonia ($NH_3 + NH_4^+$) at pH values close to neutral (where NH_4^+ predominates), reflecting solubility control by ammonium phosphates (e.g., struvite; *SI Appendix*, Fig. S3).

In contrast to dissolved carbonate species and ammonia, the H_2 activity, indicating the redox state of the system, and temperature have minor effects on P concentration in the modeled Enceladus ocean water (*SI Appendix*, Fig. S4 and S5). Although the bulk ocean is expected to be near 0 °C, it is strongly suspected that there is hydrothermal activity in Enceladus's rocky core at elevated temperatures (>50 °C) (33). However, elevation of temperature has minimal effects on phosphorus concentration (*SI Appendix*, Fig. S7), and low-temperature water–rock reactions are expected to dominate the P budget in Enceladus's ocean assuming that fluid flow at the seafloor is dominated by low-temperature transport, as on Earth (*SI Appendix*, section S5). In comparison to temperature, increasing concentration of dissolved silica appears to decrease the P concentration, particularly if the silica concentration can reach very high values and the pH is less than ~9 (*SI Appendix*, Fig. S9).

Long-term phosphate burial on Earth is usually linked with fluorine via the formation of sparsely soluble fluorapatite [$Ca_5(PO_4)_3F$] or its precursor phases (34, 35). Lacking a measured value for the concentration of fluoride in Enceladus's ocean from Cassini data (14, 15), we considered cases with and without fluorine in the chemical system (*SI Appendix*, sections S1 and S3.1 and Table S4). In the former case, sufficient fluoride would decrease the P concentration owing to the lower solubility of fluorapatite compared with other phosphate minerals,

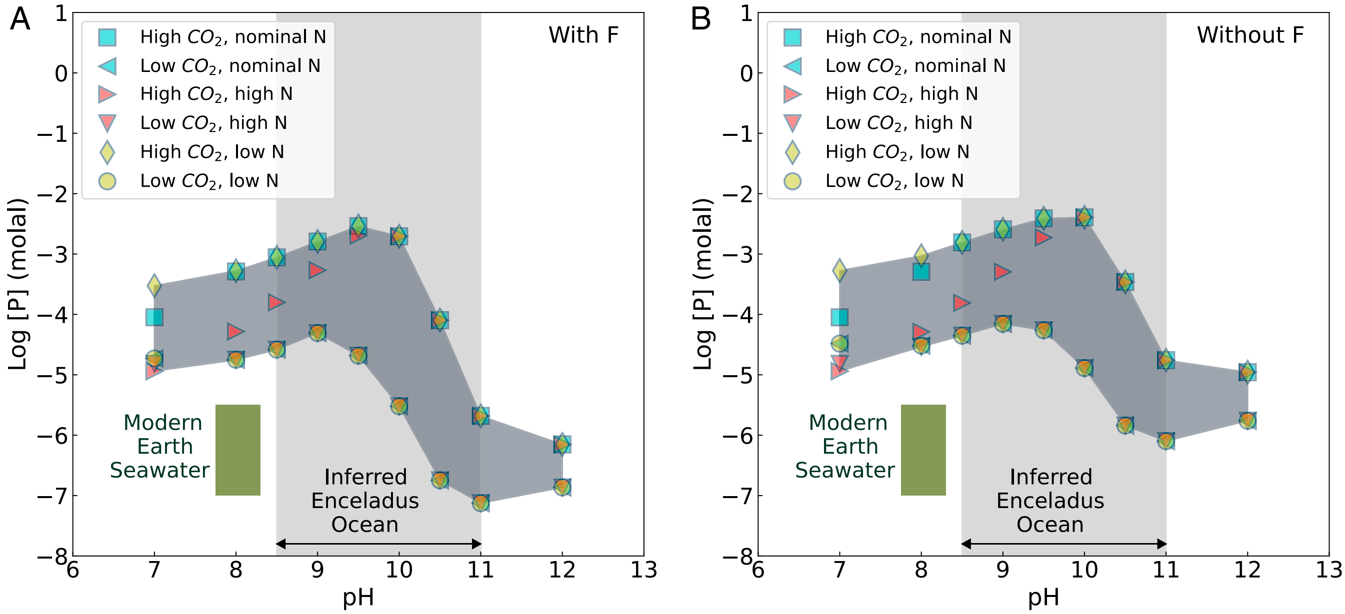

Fig. 2. Predicted concentration of orthophosphate (mainly HPO_4^{2-}) in Enceladus's ocean depending on if (*A*) fluoride is sufficiently abundant or (*B*) there is insufficient fluoride in the ocean–seafloor system to affect the oceanic abundance of P. Variation of dissolved P is controlled by the solubility of the least soluble P-bearing minerals (*SI Appendix*, Fig. S3), which is largely affected by the variation of major cations (*SI Appendix*, Fig. S2). Symbols show different cases for the concentrations of total carbonate species and total ammonia (*SI Appendix*, Table S2). The inferred pH range of Enceladus ocean water (light gray shading) also comes from interpretations of Cassini data (14, 20, 22, 31, 32). The dark gray band indicates the range of P concentration that is implied by the present modeling of water–rock equilibrium. The P concentration of modern Earth seawater (olive green box) is from Berner and Berner (19).

including OH- and Cl-apatites (Fig. 2*A* and *SI Appendix*, Fig. S3 and Table S3). However, given the relative abundances of fluorine and phosphorus in the solar system (36), even if all fluoride on Enceladus is in fluorapatite this mineral would only take up about 30% of the P budget derived from chondritic material. We do not assume that magmatic processes have produced rocks that are enriched in fluoride. Igneous differentiation would produce a metal inner core and lead to an enrichment in potassium in evolved magmas that could be emplaced at/near the seafloor. However, Enceladus's moment of inertia factor (∼0.335) appears to be too large to permit the existence of a dense inner core (37), and the K/Na molar ratio in the ocean may be too small ($\lesssim$0.1) to support a significant enrichment of K at/near the seafloor. Because there is a lack of evidence for magmatic processes that could locally increase the F/P ratio, it seems unlikely for fluorapatite solubility to be the dominant control of P at Enceladus's seafloor. The phosphate concentration in Fig. 2*A* can therefore be taken as a potential lower limit for Enceladus's ocean. Nevertheless, in both cases dissolved phosphorus is inferred to reach concentrations higher than or at least similar to those in modern Earth seawater [$10^{-5.5}$ to 10^{-7} molal (19)] (Fig. 2 and *SI Appendix*, Fig. S2). It should be noted that we did not model the possible roles of organic phosphorus (38) or other reduced inorganic phosphorus species (39). If any metastable, reduced phosphorus is present in the Enceladus ocean, then the concentration of total dissolved phosphorus would be higher than our estimates.

The high concentration of phosphate up to 10^{-2} molal is mainly caused by low concentrations of divalent cations in (bi)carbonate-rich and alkaline Enceladus ocean water (14, 21). The concentrations of these cations are limited by the precipitation of carbonate and phyllosilicate minerals (*SI Appendix*, Fig. S3). Consistent with these results, high concentrations of dissolved phosphate (as well as corresponding low concentrations of divalent cations together with similar Ca/Mg carbonate mineral precipitates) have been reported in alkaline and carbonate-rich lake waters on Earth (40–43). Moreover, the nearly linear relationship between log [total P] and log [total carbonate] in modern alkaline lakes (40, 41) is consistent with our model (*SI Appendix*, Fig. S8 and section S3.2). This resonates with the notion that modern alkaline, carbonate-rich waters may be analogous in major ion composition to Enceladus's "soda ocean" (14, 31), although the analogy is imperfect since terrestrial soda lakes are in contact with an atmosphere and subject to locally enhanced evaporative concentration.

Soil science provides additional context that reinforces our finding that the chemistry of Enceladus's ocean is primed to make phosphate minerals unusually soluble. The commonly used "Olsen method" for the analysis of phosphate in terrestrial soils is to extract it using a 0.5 M sodium bicarbonate solution at pH 8.5 (44). These conditions extract phosphate from minerals by removing calcium from the aqueous solution via carbonate mineral precipitation. This is the same application of Le Chatelier's principle that yields abundant dissolved phosphate in our geochemical model of Enceladus's ocean (*SI Appendix*, Figs. S2, S3 and S8). Indeed, the general conditions of the "Olsen method" are similar to those inferred for the ocean of Enceladus (pH ∼8.5 to 11, ∼0.01 to 0.1 molal $HCO_3^- + CO_3^{2-}$) (14, 21).

The inference of a P-rich Enceladus ocean is also supported by laboratory experiments that demonstrate significant aqueous leaching of phosphate from the Murchison and Allende carbonaceous chondrites. In the most extensive study, Mautner and Sinaj (45) reported that phosphate is readily leached, and the extracted concentration increases with solid/solution ratio and starts to level off at ratios between 0.1 and 0.4 $kg \cdot L^{-1}$. The equilibrium P concentration was found to be ∼0.15 mM at 20 °C and pH 7.4 to 7.9. This is relevant to Enceladus as the ocean water chemistry appears to be rock-buffered at a similarly high rock/water ratio of ∼0.3 to 1 $kg \cdot L^{-1}$ (20), probably because Enceladus's core is so porous (4, 29). While the experimental conditions of the previous leaching experiments do not exactly match Enceladus ocean conditions, they show that a relatively high concentration of dissolved phosphate can be obtained by simple water extraction of chondritic rock. Also, the consistency between results where the experiments and our model partially overlap at circumneutral pH (Fig. 2) can be seen as a successful empirical test of our model for chondritic systems.

Our results seem to be at odds with earlier simulations that predicted less than 10^{-10} molal orthophosphate (16, 17), which was found to be due to the extremely low solubility of whitlockite [β-$Ca_3(PO_4)_2$]. The large disagreement in P concentration is attributed to a substantial discrepancy of thermodynamic data for whitlockite between the equilibrium constant in the previous models [log $K_{sp} = -50.98$ at 25 °C for $Ca_3(PO_4)_2 \rightarrow 3Ca^{2+} + 2PO_4^{3-}$] (16, 17) and that from actual solubility experiments [log $K_{sp} = -28.92$ at 25 °C for the same reaction with solubility $>10^{-4}$ molal P at circumneutral to alkaline pHs (46–48); *SI Appendix*, section S6]. We adopted the latter value because it is most consistent with the process that we are modeling—phosphate mineral equilibration with water. To gain additional insight, we forced the former equilibrium constant for β-whitlockite into our code and obtained extremely low solubilities of dissolved P (10^{-15} to 10^{-10} molal; *SI Appendix*, Fig. S10), similar to the results of previous models (16, 17). In this case, we also found that the P concentration is controlled by the solubility of whitlockite under a wide range of conditions; in these test runs, all other P minerals were extremely undersaturated, including merrillite, which was experimentally shown to be less soluble than whitlockite (48). Previous treatments overestimated the stability of whitlockite. The present model, incorporating the latest published constraints on Enceladus's ocean water chemistry, as well as an internally consistent thermodynamic database that is tailored to P species and minerals (*SI Appendix*, Tables S1 and S3), should provide a more realistic representation of P availability that is determined by mineral solubility in Enceladus's ocean.

Our estimates also differ from results that were based on scaling fluxes of the P cycle on the modern Earth to Enceladus (18). However, there are fundamental differences between Enceladus and Earth in terms of continuous production of "fresh" seafloor igneous rocks on Earth vs. the likely presence of unrecycled, already-altered rocks at the seafloor of Enceladus (20) and more carbonate-rich ocean water on Enceladus than on Earth (14) (*SI Appendix*, Fig. S8). One should note that removal of orthophosphate through surface adsorption onto ferrihydrite is a major P sink for oxidized modern Earth seawater (49), but this process may not be relevant to reduced ocean water on Enceladus. Green rust [e.g., $Fe_6(OH)_{12}(CO_3,SO_4)$] has been proposed as a major metastable phase in Fe(II)-rich early Earth seawater (50) and can remove phosphate (51). However, green rust is not thermodynamically stable and will eventually transform into more stable phases, e.g. greenalite or siderite (50, 52) (*SI Appendix*, section S4). Our geochemical model suggests favorable formation and persistence of carbonate minerals and phyllosilicates at Enceladus's seafloor (*SI Appendix*, Fig. S3). Surfaces of these minerals will be net negatively charged because their points of zero charge are lower than the inferred pH of Enceladus ocean water (*SI Appendix*, Table S7). Consequently, there should not be significant adsorption of phosphate on mineral surfaces at Enceladus's seafloor (53) (*SI Appendix*, section S4).

A liquid water ocean might have existed for tens of million to several billion years inside Enceladus (26–28). Given this potentially long history, dissolution of phosphates and other minerals can be expected to release considerable amounts of phosphorus (together with other dissolved constituents) into the ocean, perhaps allowing these minerals to equilibrate with the ocean. As an initial assessment, equilibrium seems plausible in terms of mass balance; i.e., only small quantities of secondary minerals need to be dissolved for their saturation states to be reached. For example, the total dissolution of core rock would release more than 100 mmolal P (*SI Appendix*, Table S6), but our simulations predicted no higher than millimolal levels of dissolved P at equilibrium (Fig. 2). This dissolved P inventory is equivalent to ~1% of the core's mass, or the P content in a subseafloor rock layer that is less than ~0.5 km thick (for comparison, the radius of Enceladus's core is thought to be around 190 km). Multivalent cations (Ca, Mg, Fe, and Si) affecting P solubility would similarly need only a thin layer of rock to exchange elements with the ocean. Because the required extents of rock exposure to ocean water are minimal, it appears that physical access of rock to water should not preclude equilibrium. Therefore, the actual equilibration period for P and its controlling metals should be much less than the complete serpentinization duration of Enceladus's core (~10^8 y) (54, 55). However, phosphates and other minerals in rock would still need to dissolve at geologically sufficient rates for species concentrations in the ocean to reach equilibrium values.

To further test if such equilibria can be reached at the present time, we estimated kinetic timescales of grain dissolution of relevant minerals on Enceladus. First, we calculated a halfway-to-equilibrium timescale for the dissolution of major phosphate minerals commonly observed in chondrites (56) (*Methods* and *SI Appendix*, Tables S4 and S5). These calculations assume that ocean water circulates through a porous and permeable subseafloor aquifer layer (0.6 to 20 km thick) of Enceladus's core and phosphate mineral grains within this layer dissolve at rates based on laboratory studies. The results suggest that the half-time for dissolution of phosphate minerals to reach 1 mmolal in the Enceladus's ocean is less than 10^5 y (Fig. 3), much shorter than the expected lifetime of Enceladus' ocean (10^8 to 10^9 y).

We performed a second set of kinetic calculations to determine whether the other minerals in our model would dissolve fast enough so that their equilibria can indirectly affect the phosphorus concentration. These simpler calculations for the total dissolution lifetime of spherical mineral grains can serve as an indicator of whether slow kinetics would inhibit the attainment of equilibrium (57). We find that these timescales are less than 10^8 y even at 0 °C and may be much shorter than this if secondary silicates in Enceladus's core are analogous to the very fine-grained matrix (<1 to ~10 μm grain radii) (58) that is the dominant component of aqueously altered chondrites (*SI Appendix*, Fig. S12). The above findings jointly support (but of course do not guarantee) the assumption of equilibrium for phosphate, suggesting that the results in Fig. 2 and *SI Appendix*, Figs. S2 and S3 are applicable to present knowledge of Enceladus's ocean. Note that there remains uncertainty as to whether merrillite would dissolve sufficiently fast to equilibrate with the ocean because rate data do not exist where it is predicted to be most stable (pH >9 to 10; *SI Appendix*, Figs. S3 and S11). However, the general trend in our kinetic analyses is that minerals with ionic salt structures dissolve relatively quickly (Fig. 3 and *SI Appendix*, Fig. S12). Merrillite [$Ca_{9.5}Mg(PO_4)_7$] can be expected to behave similarly. We also note that even deeper fluid circulation is plausible and may be linked to the prodigious heat output of Enceladus (29), but we chose to focus on shallower circulation because it is less difficult (less rocky material to flow through). On the other hand, if deep fluid circulation is sufficiently widespread and rapid enough to influence the ion

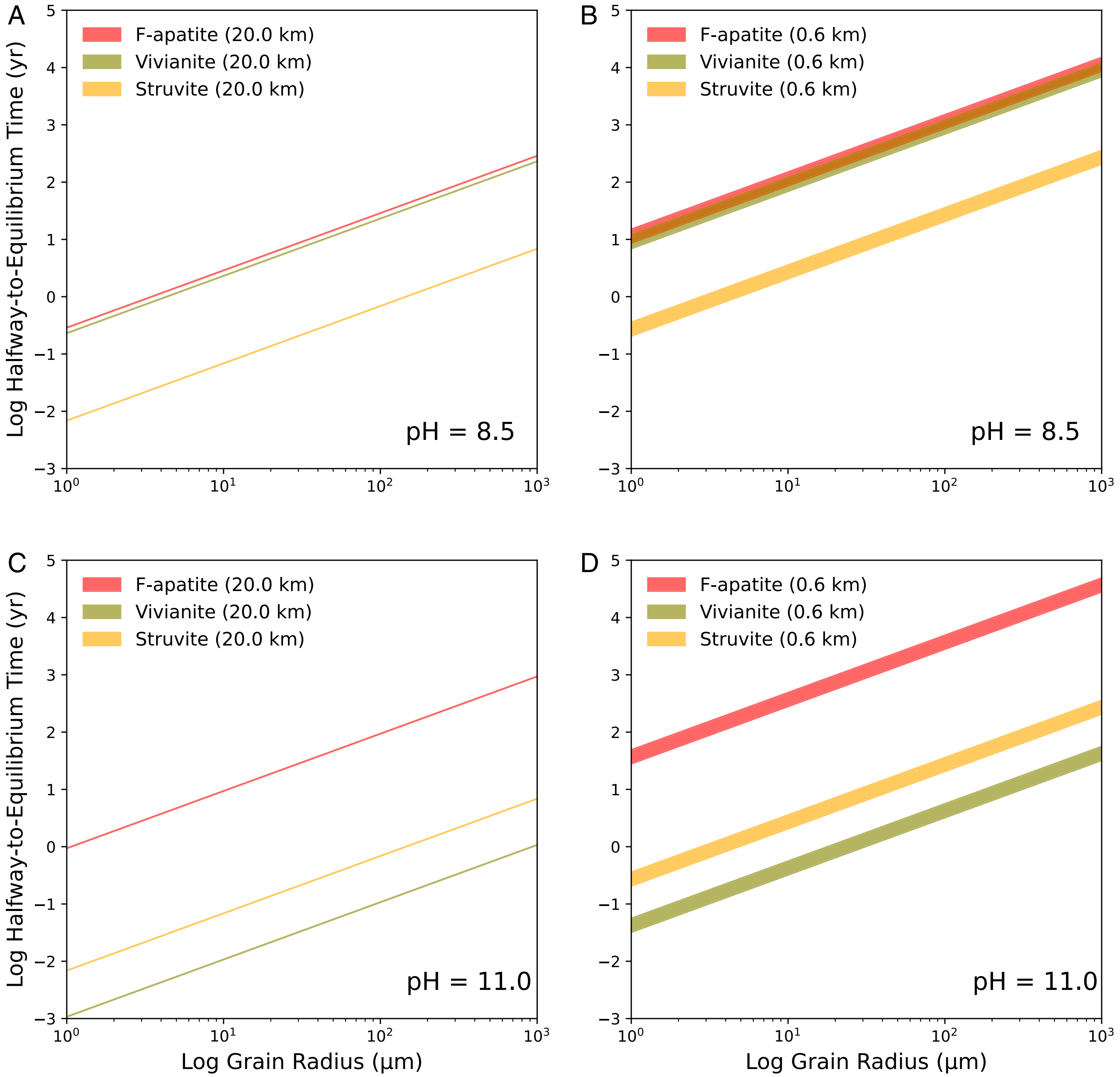

Fig. 3. Amount of time that is required for the dissolution of P minerals to proceed halfway to equilibrium as defined by Eq. **6**. into Enceladus's ocean at 0 °C, as a function of the grain radius of P minerals and thickness of a permeable subseafloor layer [0.6 to 20 km (20, 78)]. Top and bottom panels correspond to limiting values of the observationally constrained pH range (14, 20, 22, 31, 32). Shaded areas indicate the dissolution timescale with a 20-km- (*A* and *C*) or 0.6-km- (*B* and *D*) thick permeable layer. The vertical extent of shading reflects variation in mineral surface area (i.e., decreasing grain size) as mineral dissolution proceeds (*Methods*). The equilibrium concentration of dissolved P is set to be 1 mmolal to illustrate a conservative case (Fig. 2 and *SI Appendix*, Fig. S2) with a relatively long timescale.

composition of the ocean, then phosphate should reach equilibrium even faster because ocean water would have access to additional phosphate mineral grains.

Implications

Our finding that phosphate should be abundant in Enceladus's ocean implies that another major component of habitability is likely to be satisfied there. Indeed, phosphate becomes limiting for the growth of terrestrial hydrogentrophic methanogens below ~10^{-8} to 10^{-6} molal phosphate (59, 60), and this requirement can be easily satisfied by the inferred high phosphate levels in the Enceladus ocean (Fig. 2 and *SI Appendix*, Figs. S2, S4 and S5). If life exists in the Enceladus ocean, its activity could promote the bioavailability of phosphorus. For instance, life cannot only synthesize organic P and increase the concentration of total dissolved P but also recycle organic P in the ocean column (61, 62). Finding appreciable abundances of organic P-bearing species containing phosphate ester and particularly phosphoanhydride bonds would likely implicate biosynthesis, since a state of significant disequilibrium would be implied, given what we know about conditions in Enceladus's ocean (*SI Appendix*, section S7). In addition, life's activities can facilitate the process of reaching thermodynamic equilibria between water and minerals via ligand-promoted mineral dissolution (63, 64) or biologically mediated mineral precipitation (65).

Further analysis enables a deeper perspective on what could ultimately limit the habitability of Enceladus's ocean. It does not appear to be CHNOPS elements or energy sources, if the tentative detection of H_2S (9, 10) and our predictions of phosphorus availability (Fig. 2) can be confirmed via either further analyses of Cassini Cosmic Dust Analyzer data or detection by future missions. Measurements of sodium phosphate salts would enable direct testing of our geochemical model predictions (Fig. 2 and *SI Appendix*, Fig. S8), and the oceanic concentration of P in relation to other biogenic elements would allow quantitative assessment of whether P or a different element is a limiting nutrient for putative life. We do not expect reduced P species to be found if the P–O–H system has reached redox equilibrium in Enceladus's ocean (Fig. 1 and *SI Appendix*, Fig. S1). Our geochemical model can also be tested by making measurements of additional elements (Ca and Mg) that are expected to be controlled by mineral dissolution equilibria (16, 20) (*SI Appendix*, Figs. S2 and S3). By determining the ocean's major ion chemistry, pH, and phosphate concentration, mineral saturation indices could be evaluated to constrain the seafloor mineralogy, including the most stable P-hosting phase. This would be valuable for advancing our understanding of the geochemical evolution of the ocean–seafloor system on Enceladus.

Cassini data show that molecular hydrogen (4) and organic compounds (7–10) represent substantial sources of electron donors for microbes including methanogens. The availability of electron acceptors (oxidants), however, is potentially limiting. Oxidant (O_2 and H_2O_2) production from radiolysis of water molecules is relatively slow on Enceladus, and there may be additional complications such as discontinuous transport of oxidants from the surface to the ocean or scavenging of reactive oxygen species by organic compounds in the ocean (66). The only abundantly available oxidant that has been observed is inorganic carbon in the form of carbonate species. This oxidant appears to be sufficient to allow hydrogenotrophic methanogenesis ($CO_{2,aq} + 4\ H_{2,aq} \rightarrow CH_{4,aq} + 2\ H_2O$) that would provide enough energy to support methanogens (4–6). However, the potential to sustain metabolisms that rely on other oxidants may be more restricted on Enceladus.

An additional limiting factor for possible life may be transition metals. These are needed to catalyze biological redox reactions including methanogenesis (67), which uses nickel-based enzymes (68). The availability of transition metals in the Enceladus ocean may be scarce because of low solubilities of their mineral forms in alkaline, carbonate-rich, and reduced ocean water (e.g., iron, nickel, zinc, and molybdenum) (17, 31). If this effect is important, then the most habitable zone on Enceladus may be the water–rock interface where these elements are most accessible. Alternatively, there may be potential to mobilize metals via chelation in an organic-rich ocean (8). These considerations emphasize the next step of thinking beyond CHNOPS and also in terms of local environments as we more deeply probe the prospects for life in Enceladus's ocean (69).

Methods

Dominant Form of Dissolved Phosphorus. Equilibrium constants for the phosphorus Pourbaix diagram (Fig. 1) were computed with the code SUPCRT92b (70), using the most recently updated revised Helgeson–Kirkham–Flowers (HKF) equations-of-state parameters taken from the database of the Deep Earth Water model (71). Thermodynamic properties of aqueous phosphorus species correspond to 0 °C and 70 bars. Equilibrium boundaries between aqueous species were calculated using their Gibbs free energies of formation at the seafloor pressure ($\Delta G^{\circ}_{f,\,P}$) and assuming equal activities of the two P species separated by each boundary. Values of $\Delta G^{\circ}_{f,\,P}$ were calculated using standard Gibbs free energies of formation (ΔG°_{f}) and other thermodynamic properties (standard partial molal entropy, volume, heat capacity, and a_1-a_4, c_1-c_2 and ω parameters) for the revised HKF equations of state for aqueous species, which are provided in *SI Appendix*, Table S1.

Numerical Simulation of Enceladus Ocean Chemistry. Thermodynamic calculations were performed using the aqueous speciation, complexation, and solubility code EQ3NR (72), except for the temperature sensitivity tests which adopted output of EQ3NR at 0 °C as input of EQ6 for a heating simulation (*SI Appendix*, sections S1 and S3.5). EQ3NR determines which minerals should be present at equilibrium and assumes that enough rock is available to prevent complete dissolution of those minerals (*SI Appendix*, Fig. S3 and Table S6) during the process of reaching equilibrium. Previous reaction path modeling suggests that the currently constrained chemistry of Enceladus's ocean is consistent with the results of chondrite alteration by CO_2-rich fluids at low water/rock mass ratios (between 1 and 3) (20). The thermodynamic database used in the present calculations was built using established data for aqueous species (73) and minerals (74–76). A large number of aqueous species and minerals of phosphorus were included in the database (*SI Appendix*, Tables S1 and S3), and we verified that white P at 25 °C is the reference state for all of their apparent Gibbs energies and enthalpies. While the present database is extensive, one should be mindful that it is possible that some unfamiliar P mineral could form in this potentially exotic extraterrestrial environment, but because of a lack of thermodynamic data it would not be represented by our model.

The Enceladus ocean chemistry model was parameterized based on current plume constraints on ocean composition; i.e., total concentrations of Cl^- and carbonate species, ratios of Na/K, $H_{2(aq)}/CO_{2(aq)}$, and $\Sigma NH_3/CO_{2(aq)}$, at 0 °C (*SI Appendix*, Table S2). This is the same type of approach as that used by Waite et al. (4), and it is extended here to include mineral equilibria. We adjusted the redox state of the system (e.g., log $fO_{2,g}$ [oxygen fugacity]) to reproduce the observationally constrained H_2 molality (∼activity). Na^+, as the dominant cation in the ocean, provides charge balance [the calculated strength varied from 0.08 to 0.49 molal; this is within the range of applicability of the extended Debye–Hückel equation that is used by EQ3NR to account for nonideal solution behavior of ions (72)]. For multivalent cations, we iterated the model to reach the levels with the lowest solubilities of their corresponding secondary minerals commonly observed in aqueously altered chondrites (usually carbonate or phyllosilicate minerals; *SI Appendix*, Table S4), e.g. magnesite (at lower pH) and talc (at higher pH) for Mg^{2+}. This state of lowest solubility is equilibrium, where no alternative mineral is supersaturated. Silica concentration was nominally set to be at the solubility of quartz, consistent with recent estimates (20) (*SI Appendix*, sections S1 and S3.6). We found that no other silicate minerals were supersaturated in this chemical system. Due to a lack of knowledge on the fluorine abundance in Enceladus ocean water, we considered two endmember systems: one without and one with fluorine. The concentration of fluoride in the latter calculations was set to whichever is lower between the solubility of fluorite and the value for comparable leaching of F^- and Cl^- from rock of CI chondritic bulk composition (36). To estimate the concentration of dissolved phosphate over a wide range of pH values (7–12), we iterated the model to find the phosphate mineral of lowest solubility (*SI Appendix*, Figs. S2 and S3).

In addition to the above-mentioned simulations under the observationally constrained conditions, we tested the effects of key parameters (e.g., carbonate, ammonia, and temperature) on the equilibrium concentration of P in Enceladus's ocean under a much broader range of environmental conditions (*SI Appendix*, sections S1 and S3). Note that organic nitrogen species (amines) and organic acids were not included as sources of additional ions in our model because the specific species and their concentrations are too uncertain. We also did not consider redox equilibration between C and N species (e.g., CO_2–CO, N_2–NH_3) because redox reactions are presumably kinetically inhibited in the cold bulk ocean of Enceladus. However, these exclusions do not affect the chemistries of carbonate and ammonia, which are determined by plume values in our geochemical model (*SI Appendix*, Table S2).

Our database corresponds to 1 bar total pressure because it is conventional for aqueous geochemical databases to tabulate equilibrium constants at this pressure for temperatures below 100 °C. In reality, maximum pressures in Enceladus's ocean will be higher, ranging from 20 to 70 bars depending on the depth (21, 77). However, as shown in Fig. 1, pressures up to 70 bars have little influence on the aqueous speciation of phosphorus. Furthermore, the pressure effect on solubilities of P minerals is within a factor of 2.5 (*SI Appendix*, Fig. S6), much smaller than the effects of compositional changes (Fig. 2 and *SI Appendix*, Figs. S2, S4 and S5). More importantly, increased pressure makes P minerals more soluble (*SI Appendix*, section S2 and Fig. S6), supporting the availability of abundant P in Enceladus ocean water.

P-Releasing Kinetics during Alteration of the Enceladan Seafloor. It is assumed that there is a porous and permeable layer directly below Enceladus's seafloor where element exchange between rock and ocean water occurs. On Earth, this type of interaction occurs in the upper oceanic basement, and the thickness of this aquifer layer is ∼0.6 km (78). However, ocean water is likely to reach greater depths into the seafloor of Enceladus. Geochemical modeling indicates that the upper part of the rocky core has been significantly carbonated via interaction with CO_2-bearing ocean water down to a depth of at least ∼20 km below the seafloor (20). Geophysical modeling suggests that both cool and warm/hot fluids can be transported through the entire core (29, 79). Here, we consider a more conservative range of 0.6 to 20 km for the aquifer layer thickness to estimate upper limits on the timescale for phosphate minerals to equilibrate with ocean water.

The volume of the permeable subseafloor layer is

$$V_{aquifer} = (4/3) \times \pi \times \left(R_c^3 - r^3\right), \tag{1}$$

where R_c = core radius [∼190 km; Waite et al. (4); see also ref. (77)] and r = radius at the bottom of the permeable layer. Given ϕ = water-filled core porosity [∼27%; Waite et al. (4); see also ref. (29)], the fraction of this volume that is rock is $1 - \phi$. The mass of rock in the permeable layer is $m_{rock} = \rho_{rock} \times V_{rock}$, where ρ_{rock} = rock density [∼3.0 g/cm^3; Waite et al., (4)]. The corresponding mass of P in the rock is $m_P = m_{rock} \times c_{P,rock}$, where $c_{P,rock}$ represents the mass fraction of P in rock in Enceladus's core, suggested to be similar to that in CI carbonaceous chondrites [920 ppm (36)]. We note that a different assumed carbonaceous chondrite analog of Enceladus rock would provide a similar abundance of P as this quantity exhibits little (<10%) variation among carbonaceous chondrites (80).

Assuming that all P in the permeable layer that interacts with the ocean is in a single host mineral (e.g., apatite, struvite, or vivianite), the total amount of P in this layer can be converted into a mineral volume (V_{min}; cubic meters) using available data of molar mass and mineral density (*SI Appendix*, Table S5). Further assuming that the mineral grains are spherical with x_{grain} as the radius, the total surface area (A) of P minerals is

$$A_{min} = 3V_{min}/x_{grain}. \tag{2}$$

The grain size of P minerals in aqueously processed terrestrial and chondritic samples that may be relevant to Enceladus's seafloor ranges from <10 to 100s of micrometers (65, 81). Here, we consider a wide range of grain size; i.e., 1 μm to 1 mm.

Dissolution kinetics of phosphate minerals were compiled from previous experimental results (*SI Appendix*, Table S5 and Fig. S11). The dissolution rate is defined as the amount of mineral that dissolves per unit surface area per second (R_+; moles of released P·m^{-2}·s^{-1}). We adopted laboratory-based rates because they provide a useful starting point with well-characterized values. It is important to be aware that dissolution rates inferred from field measurements on Earth can be much different from those measured in the laboratory, owing to the complexity of geologic environments (82, 83). However, we do not (yet) understand the kinds of complexity that could change dissolution rates on Enceladus. In the laboratory, the dissolution rates of phosphate minerals are usually measured at 25 °C. According to the available activation energy values for dissolution reactions of fluorapatite and struvite (*SI Appendix*, Table S5), the dissolution rate at 0 °C is about five times less than that at 25 °C. This factor is applied to vivianite since dissolution rate data are not currently available for it at 0 °C. The net rate of dissolution of P minerals can be represented by

$$R_{net} = R_+\left(1 - \frac{[P]}{[P]_{eq}}\right), \tag{3}$$

where $[P]$ and $[P]_{eq}$ are real-time and equilibrium concentrations of dissolved phosphate, respectively. This equation provides a simple accounting for the reverse reaction of precipitating the phosphate mineral of interest as the system approaches equilibrium (84). It is simplified by the assumption that the background electrolytes in Enceladus's ocean (mainly NaCl) remain constant over the course of phosphate mineral dissolution, so that the ratio of concentrations in Eq. **3** is similar to the ratio of appropriate activities. From this first-order formulation, the P concentration (molal) in Enceladus's ocean would evolve according to

$$\frac{d[P]}{dt} = \frac{A_{min}R_+}{m_{ocean}}\left(1 - \frac{[P]}{[P]_{eq}}\right), \tag{4}$$

where A_{min} stands for the total surface area of phosphate minerals that exchange P with the ocean, as estimated above, and m_{ocean} refers to the mass of Enceladus's ocean [∼2 × 10^{19} kg (77)]. For simplicity, assuming that A_{min} stays constant (i.e., the mineral grain radius does not significantly decrease during partial dissolution) and the initial concentration of orthophosphate in the ocean was zero, then the integrated rate equation would be

$$-[P]_{eq}\ln\left(1 - \frac{[P]}{[P]_{eq}}\right) = \frac{A_{min}R_+}{m_{ocean}}t. \tag{5}$$

The timescale (years) to reach halfway-to-equilibrium is then

$$t_{1/2} = \frac{-m_{ocean}[P]_{eq}}{A_{min}R_+}\ln(1 - 0.5). \tag{6}$$

On the other hand, A_{min} would decrease noticeably due to a high degree of P-mineral dissolution if the permeable layer of the core is very shallow (e.g., 0.6 km). To bound this effect, we considered the mass balance of P at an ocean concentration of $[P] = [P]_{eq}/2$. We calculated the mass of phosphate minerals that would dissolve into Enceladus's ocean to reach this concentration, and then calculated the remaining mass of phosphate minerals in the aquifer layer (designated by $m_{P,1/2}$). The corresponding grain radius and total surface area of phosphate minerals in the aquifer layer are given by

$$\frac{m_{P,0}}{x^3_{grain,0}} = \frac{m_{P,1/2}}{x^3_{grain,1/2}} \tag{7}$$

and

$$\frac{A_{min,0}}{x^2_{grain,0}} = \frac{A_{min,1/2}}{x^2_{grain,1/2}}, \tag{8}$$

where subscript 0 indicates the initial state of the system and subscript 1/2 refers to the halfway-to-equilibrium point. We used these equations to convert from $m_{P,1/2}$ to $A_{min,1/2}$ and evaluated Eq. **6** for the new smaller surface area. The resulting halfway-to-equilibrium time can serve as an upper limit (Fig. 3) as it is based on the minimum total surface area.

Above, we quantitatively evaluated the dissolution rates of phosphate minerals, as they are known to be important P-containing secondary phases in aqueously altered chondrites (*SI Appendix*, Table S4), and Enceladus's core is thought to be heavily altered (i.e., hydrated). However, prior to the formation of phosphate minerals, there were probably anhydrous rocks on Enceladus perhaps like ordinary chondrites or other ultramafic rocks, such as peridotite. The implication is that some P could have been dispersed within olivine, and the majority of accreted P most likely resided in metal phosphides, such as schreibersite. It is notable that the dissolution rate of olivine minerals, e.g., forsterite, is experimentally shown to be faster than that of apatite at alkaline pHs relevant to Enceladus ocean water (85, 86). Metal phosphides are very reactive and if present inside Enceladus would dissolve in days (39). We conclude that the estimated timescales of P availability will be conservative not only to the attainment of equilibrium with secondary phosphates, but also with respect to the initial stage of aqueous alteration.

Data, Materials, and Software Availability. All study data are included in the article and/or *SI Appendix*.

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Supplementary Information for
Abundant phosphorus expected for possible life in Enceladus's ocean.

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- Tables S1 to S7
- SI References

S1. Additional model description

The Cosmic Dust Analyzer (CDA) aboard the Cassini spacecraft detected Na, Cl, and (bi)carbonate as the major salt species of icy plume particles from Enceladus (1). Levels of chlorine are suggested to be between 0.2 mole/kg H_2O or molal (at high carbonate) and 0.05 molal (at low carbonate) (1), which were adopted in our model (**Table S2**). It is notable that this level of Cl is generally higher than the maximum level that would be provided by complete dissolution of Enceladus core material in ocean water (**Table S6**); however, additional Cl could have been accreted in volatile/icy forms rather than solely with rock (2, 3). Na^+ is found to be the dominant cation in salty particles and thus was set to be the charge balance species in our geochemical model. On average, K was suggested to be roughly 100-200 times less abundant than Na in plume particles (1). Here, we set the total concentration of K as 100 times less than that of Na.

Total carbonates ions (HCO_3^- + CO_3^{2-}) are suggested to be 0.01-0.1 molal in Enceladus ocean water (1), which were adopted in this model as low and high C cases, respectively. Note that this parameter is different from dissolved inorganic carbon ($CO_{2,aq}$ + HCO_3^- + CO_3^{2-}) and carbonate alkalinity (HCO_3^- + $2\times CO_3^{2-}$), which are typically reported in geochemical field studies. However, total carbonates is the parameter that was derived from CDA data. In addition, to assess the effect of total carbonate level on P level, we conducted sensitivity tests by varying total carbonate level from 0.001 to 0.5 molal. In those sensitivity tests, total Cl concentration was set to be 2 times that of total carbonate to maintain consistency with the results of Postberg et al. (2009) (1). Based on data from the Ion Neutral Mass Spectrometer (INMS) aboard the Cassini spacecraft, it was suggested that the $H_{2,aq}/CO_{2,aq}$ ratio in Enceladus's ocean is 0.5-4.7 (4). In our model, we varied log $fO_{2,g}$ (oxygen fugacity) to reach the target $H_{2,aq}/CO_{2,aq}$ ratio (0.5 for low H_2 case; 4.7 for high H_2 case) in the simulated Enceladus ocean water.

Nitrogen in Enceladus ocean water is reported to be predominantly reduced valence (N(-III)) with a N/CO_2 ratio of ~1.5 in the plume gas (4). Here, we define the level of N in terms of total dissolved ammonia (NH_3 + NH_4^+) instead of NH_3 only as 1.5 times that of $CO_{2,aq}$, because interconversion between ammonia species is expected to be much faster than interconversion between CO_2 and carbonates over the degassing timescale (4). In addition, we also varied N (total N/CO_2 ratio from 0.15 to 15) to evaluate the effect of N abundance on the P concentration.

There is a lack of observational data on the abundances of divalent cations (Ca, Mg, and Fe) in the Enceladus ocean (1). However, levels of these cations can affect P concentration because they are major components of common P-minerals whose solubilities can be shifted by the common ion effect. Various lines of evidence suggest the occurrence of water-rock interactions in Enceladus's seafloor (1, 4, 5), which have altered primary silicate minerals into secondary silicate/carbonate/hydroxide minerals as observed in chondrites (6, 7). In addition, molecular $H_{2,g}$, likely generated by water-rock reactions, was detected to be a major species of the plume gas (4), suggesting an overall reducing Enceladus ocean. Under this condition, Fe exists predominantly in reduced form, i.e. Fe(II). In this study, we assumed that activities/concentrations of the key divalent cations are controlled by dissolution of the least soluble common secondary minerals (e.g. carbonates and phyllosilicate minerals (8)).

The fluorine concentration in Enceladus's ocean is currently unknown, but may be limited by the abundance of F in Enceladus's rocky core (**Table S6**). However, there are uncertainties in the solar abundances of halogens (9), and halogens could have been delivered to ice-rock bodies mostly as part of the icy component during accretion (2, 3). Despite these uncertainties, the accreted F/Cl ratio may stay relatively constant because of the similar chemical properties of F and Cl. Therefore, in a first approach, we estimated the F^- concentration in Enceladus's ocean water by scaling the F/Cl ratio in CI chondrite material by the appropriate Cl^- concentration for Enceladus's ocean (see above). The resulting estimate is higher than the level that is predicted by dissolving all fluorine from rocky material into the ocean (**Table S6**); therefore, it represents an upper limit. A second limiting factor for fluorine concentration is precipitation of fluoride minerals, i.e., fluorite (CaF_2) in this study. Fluorite is a common F-host mineral during hydrothermal alteration (10). Thus, fluorine concentration in our model is set to be the lower value between the solubility of fluoride minerals and the estimated level of fluorine based on conservative leaching of F and Cl.

The concentration of silica in Enceladus ocean water has been proposed to correspond to the solubility of quartz in seafloor sediments (8). These authors found that geochemical models based on equilibrium with quartz are consistent with the inferred pH of the ocean, while models with amorphous silica gave pH values that are too low. Under weathering conditions, silica is primarily released by dissolution reactions of solid silica (e.g., quartz) and silicate minerals (e.g., feldspar, olivine, and pyroxene). In the absence of biological silica precipitation, the efflux of silica from seawater is dominated by diagenetic reactions involving carbonate and clay minerals (11–13). In natural waters on Earth, the level of dissolved silica can go up to the solubility of amorphous silica, above which amorphous silica will quickly precipitate. However, in marine sediments, silica tends to transform into more stable forms, for example, opal and later quartz depending on the duration and temperature of diagenesis (12–14). As a consequence, silica concentration would decrease in pore spaces of marine sediments due to nucleation of secondary silica such as opal and reach levels close to the solubility of cristobalite during early to middle diagenesis (11). It has also been proposed that in the presence of water, amorphous silica would irreversibly transform into quartz in less than 500 Ma (15). Due to the lack of continents and thus influx of silica from continental weathering, a silica cycle on Enceladus may be predominantly controlled by transport from/to the seafloor. As the Enceladus ocean may have existed for hundreds of Ma to several Ga (16, 17), diagenetic reactions in its seafloor might have driven the silica system toward equilibrium and close to the solubility of quartz (log activity of aqueous silica in equilibrium with quartz = -4.64 at 0 °C; data from EQ3/6 (18)). Thus, we set dissolved silica to be the solubility of quartz in our nominal model runs. We also tested the effect of silica level by setting it to be the solubility of amorphous silica (log activity of aqueous silica in equilibrium with amorphous silica = -3.12 at 0 °C; data from EQ3/6 (18)), cristobalite (log activity of aqueous silica in equilibrium with cristobalite = -3.50 at 0 °C; data from EQ3/6 (18)), or chalcedony (log activity of aqueous silica in equilibrium with chalcedony = -4.34 at 0 °C; data from EQ3/6 (18)).

Total P from Enceladus's entire core of assumed CI carbonaceous chondritic composition (19) could provide up to ~100 mmole/kg H_2O if totally released into the ocean. Additional phosphorus may come from cometary volatiles (e.g. Altwegg et al., 2016 (20)), similar to halogens. In this study, we iterated the model and set dissolved phosphate to the solubility of the least soluble P-minerals in the simulated Enceladus ocean water (**Fig. S3**). Thus, our estimates may represent an underestimate of total P level, as reduced inorganic P or organic P, delivered by cometary impacts, could have added more dissolved P to the Enceladus ocean.

The temperature in our model was set to 0 °C in standard runs, representing globally ubiquitous conditions in the ice-covered ocean of Enceladus. However, geochemical evidence suggests the occurrence of hydrothermal activity, likely reaching >50 °C (21). While such activity may be localized (see **Section S5**), it is useful to understand how it could affect the availability of P in the ocean. To evaluate the potential effect of a temperature gradient on P availability, we used our 0 °C result as an input to a heating model which increased the fluid temperature to a higher value (25, 60, or 100 °C). The heating model had no mineral input but was allowed to precipitate out minerals. Therefore, the simulated P level at elevated temperatures may not be any lower than P mineral solubilities in hot fluids.

All of the thermodynamic calculations described above were conducted using the aqueous speciation and mineral solubility code EQ3NR. For the heating model, we used EQ3NR's result (at 0 °C) as an input for EQ6 which simulates aqueous speciation and mineral precipitation that would occur for an increase in temperature of up to 100 °C.

S2. Pressure effect on the model

The pressure in our model is equal to the reference pressure of 1 bar. Due to the coverage of an icy shell and overlying water column, the actual pressure of ocean water inside Enceladus may range from ~20 to ~70 bars depending on depth in the ocean. To examine the pressure effect on the model results, we calculated equilibrium constants (log K_{diss}) of dissolution reactions of major P-minerals (for example, $Ca_5(PO_4)_3F + 3H^+ \rightarrow 5\ Ca^{2+} + 3\ HPO_4^{2-} + F^-$) as a function of pressure at 0 °C. The calculations were performed by the Fortran computer code SUPCRT92b (http://www.dewcommunity.org/resources.html) (22), with thermodynamic properties of minerals from Berman (1988) (23) and apatite minerals from Zhu & Sverjensky (1991) (24). For vivianite, merrillite, struvite, and whitlockite, owing to a lack of mineral density data at both 0 °C and high temperatures, we adopted constant molar volumes of these minerals equal to the values at 25 °C and 1 bar (**Table S5**). Thus, the effect of pressure (P_{tot}) on Gibbs free energies of formation ($\Delta G_{f,1\rightarrow P}$) of the four minerals can be approximated by

$$\Delta G_{f,1\rightarrow P} = V^{\circ} \times (P_{tot} - 1), \tag{S1}$$

where V° is taken to be the mineral molar volume (cm^3/mole) at 25 °C and 1 bar. Then, the pressure effect on phosphate mineral solubility can be assessed as antilog ($\frac{(\log K_{diss}^{P} - \log K_{diss}^{P = 1\ bar})}{n}$), where *n* designates moles of P atoms released per 1 mole dissolution reaction.

The results show an overall positive effect from pressure on P mineral solubilities at pressures < 80 bars (**Fig. S6**), indicating that our modelling results at 1 bar likely represent a slight underestimate of the equilibrium P concentration in Enceladus's ocean. Pressure has little (a factor of less than 1.5 for most P-minerals) to modest (a factor of 2.3 for struvite) effects on the solubilities of P-minerals. The pressure effect is much smaller than the effects of compositional variations, which can change the results by several orders of magnitude (**Fig. 2; S2, S4 & S5**).

S3. Sensitivity tests

In addition to the standard boundary conditions constrained by Cassini mission data (**Fig. 2; S2 & S3**), we conducted sensitivity tests over a much broader range of environmental factors (fluorine, carbonate, redox state, ammonia, temperature, and silica) that could potentially affect P levels in Enceladus ocean water.

S3.1 Sensitivity to fluorine level

Our results show an overall negative effect of fluorine on P concentration due to the low solubility of F-apatite (**Fig. 2; S2 & S5**). However, fluorine is about 10 times lower in atomic abundance than phosphorus in CI material (**Table S6**); consequently, fluorapatite ($Ca_5(PO_4)_3F$) is not expected to be a predominant sink of P. Apart from fluorapatite and fluorite, fluorine also commonly substitutes for OH in hydrated silicate minerals including micas, amphiboles, and serpentine-group minerals during water-rock reactions (24, 25). If any of these minerals are abundant hosts for F on Enceladus, then there would be even less F available to influence P. Therefore, our estimates in the presence of high fluorine should serve as conservative values for dissolved P in Enceladus ocean water (**Fig. 2; S5**).

S3.2 Sensitivity to carbonate level

Based on analysis of plume ice grains from Enceladus, levels of total carbonate species were inferred to be between 0.01 and 0.1 molal (1). Our results suggest that P levels in the high C case (0.1 molal) are overall higher than in the low C case (0.01 molal) (**Fig. S2, S4 & S5**). This seemingly positive relationship between carbonate and dissolved P levels was further tested and substantiated over a wider range of carbonate concentrations (**Fig. S8**). The positive relationship and the absolute levels of dissolved P are similar to previous observations of certain modern Earth surface waters which displayed a linear correlation between log [total carbonates] and log [total P] (26, 27). These similarities reflect the same general mechanism for P-enrichment, i.e., in the presence of abundant carbonate species at alkaline pH, formation of carbonate minerals suppresses concentrations of key divalent cations (Ca, Mg, Fe) and consequently allows higher solubility of P-minerals. However, unlike Enceladus's ocean, the chemistry of terrestrial alkaline lake waters is further complicated by runoff input, high fluxes of evaporation, and/or precipitation of amorphous precursor minerals (28, 29) reflecting the rapid cycling of elements in the solar-powered surface environment of Earth. Moreover, modern soda lakes are under a strongly oxidizing atmosphere, potentially leading to the oxidation of Fe(II) rather than precipitation of Fe(II)-carbonate/phyllosilicate in anoxic settings (like Enceladus's ocean).

S3.3 Sensitivity to H_2 level

Redox state can directly influence the abundance of P in liquid water by controlling phosphorus speciation because of higher solubilities of solids containing reduced phosphorus, e.g. phosphite P(III) (30), compared with orthophosphate. However, under the inferred redox conditions of Enceladus ocean water, indicated by observed $H_{2,g}$ levels, orthophosphate was found to be the predominantly stable form of P (**Fig. 1 & S1**). In the presence of iron, redox state can also indirectly affect the availability of P, by precipitating strengite ($Fe(III)PO_4•2H_2O$) under oxidizing conditions, or vivianite ($Fe_3(PO_4)_2•8H_2O$) under reducing conditions. Under the apparent redox states of Enceladus's ocean, Fe should always be in the form of Fe(II) (31). As a consequence, variation of redox state within present boundary constraints (H_2/CO_2 ratio = 0.5-4.7; Waite et al., 2017 (4)) has minimal effects on levels of oceanic orthophosphate as shown in **Fig. S4 & S5**.

S3.4 Sensitivity to ammonia content

According to INMS data, nitrogen in the ocean of Enceladus is predominantly in the fully reduced form with an N/CO_2 ratio of about 1.5 (4). In the presence of high levels of ammonium (together with other cations), dissolved phosphate can precipitate as ammonium phosphate (e.g., struvite) (32, 33). Indeed, at relatively low pHs (7-7.5), our model shows struvite to be the least soluble (most stable) P-mineral which can maintain dissolved P at somewhat decreased levels (**Fig. 2; S2 & S3**). Furthermore, sensitivity tests of N level (N/CO_2 = 0.15 or 15; corresponding to the low or high N case, respectively) on P level showed that high levels of N would decrease P levels that are controlled by the solubility of struvite (**Fig. S4 & S5**). However, a high NH_4^+ content may not be consistent with CDA data. As an example, there is not a large peak at 18 u in Fig. 1b of Postberg et al., 2009 (1), and mass 18 peaks that can be attributed to NH_4^+-bearing salts have not been seen in other spectra of Type 3 (salt-rich) grains (Khawaja et al., 2019 supplement (34)).

S3.5 Sensitivity to temperature

Due to the fact that neutral pH varies with temperature, P levels at different temperatures were plotted against the reference pH value at 0 °C (for T = 25, 60, or 100 °C; **Fig. S7** shows the starting pH at 0 °C). Our results displayed a negligible effect of temperature on P level in Enceladus ocean water. However, this consideration is most relevant to localized fluids because high-temperature geochemical processes may not dominate the composition of the bulk ocean, assuming elements/aqueous species have low temperature sources of appreciable magnitude (see **Section S5**).

S3.6 Sensitivity to silica concentration

Phosphorus rarely precipitates with silica to form silicate minerals (18 P-Si minerals out of 449 P-minerals; data from http://rruff.info). However, silica level can affect relative stabilities of secondary silicate and carbonate minerals and thus levels of dissolved cations (e.g., Mg, Fe, and Ca). In this way, silica can indirectly influence P level. To examine effects of silica level on P level, we set dissolved silica to be at equilibrium with the most soluble silica solid – amorphous silica. Our results suggest that high silica level has a negative effect on P level at moderately alkaline pHs but a weakly positive or negligible effect at very high pH (**Fig. S9**). These effects are largely due to changing stability relationships between phyllosilicate and carbonate minerals and thus concentrations of Mg and Ca at high dissolved silica. For example, at moderately alkaline pHs (9-10) and very high silica concentration (controlled by solubility of amorphous silica), talc ($Mg_3Si_4O_{10}(OH)_2$, a common phyllosilicate formed by seafloor weathering) is found to be more stable than magnesite ($MgCO_3$) in our model, leading to a lower concentration of magnesium in modeled ocean water. In turn, solubility of calcium is predicted to increase because of solubility control by dolomite ($CaMg(CO_3)_2$). In the presence of F^-, fluorapatite ($Ca_5(PO_4)_3F$) is the least soluble phosphate mineral, whose solubility is very sensitive to calcium concentration and decreases as calcium concentration increases. In the absence of F^-, merrillite ($Ca_{9.5}Mg(PO_4)_7$) is found to be the least soluble phosphate mineral in the case of silica concentration controlled by amorphous silica solubility, instead of vivianite ($Fe_3(PO_4)_2·8H_2O$) in other runs with lower silica concentrations. At very high pH of 12, elevation of silica would have a negative effect on calcium concentration due to formation of tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) and thus indirectly favors higher solubility of calcium phosphate minerals (F-apatite in the presence of fluorine; merrillite in the absence of fluorine). Similar to the sensitivity test with fluorine, the results for high silica level may provide a conservative estimate of P levels (but still comparable to or higher than seawater on Earth), because the silica concentration in the bulk ocean is thought to be lower than the solubility of amorphous silica (see **Section S1**).

Hydrothermal activities in Enceladus's core may delivery locally high concentrations of dissolved silica (5, 21) and cause supersaturation with respect to various silica solids in a hydrothermal plume. To test its effect on P concentration, we performed additional simulations at 5 mM dissolved silica (about 5 times the solubility of amorphous silica at 0 °C and neutral pH). Similar to what we already observed in previous calculations, elevation of silica concentration would decrease the predicted solubility of P by affecting the concentrations of divalent cations (Ca, Mg, Fe) at weakly alkaline pHs ($pH < 9$; **Fig. S9**). However, at moderately alkaline to high pHs ($pH \geqslant 9$), increasing $SiO_{2(aq)}$ from amorphous silica solubility to 5 mM has negligible or weakly positive effects on P solubility. We should emphasize that even at high concentration of dissolved silica, the predicted dissolved P concentration could still reach 10^{-7} to 10^{-4} molal at pH between 8.5 to 11 (previously proposed to be relevant to Enceladus ocean water). Moreover, precipitation of amorphous silica could reach equilibrium in days (35, 36), and a hydrothermal plume is likely to be chemically distinct from the global ocean-seafloor system that is expected to govern the abundance of oceanic phosphate (see **Section S5**).

Above, we examined the effects of various environmental factors representing a larger range of possibilities than the observationally constrained nominal conditions (**Fig. 2**). In summary, pH, fluorine, carbonate, ammonia, and silica contents have either positive or negative effects on P levels in Enceladus's ocean water, whereas redox state and temperature have negligible effects. It should be noted that some sensitivity tests (e.g., relatively low or high pHs, high levels of fluorine, carbonate, ammonia, or silica) are likely to provide conservative estimates of P levels, and the actual P level can be expected to be higher than those estimates. Nevertheless, all of the estimates are higher than or close to P levels in modern Earth seawater, suggesting enough P for possible life in the Enceladus ocean.

S4. Potential effects of mineral adsorption

In the phosphorus cycle on modern Earth, seafloor weathering of basalt acts as a net sink of P mainly controlled by surface adsorption onto sedimentary minerals and burial of Ca-P minerals (37–40). The surface adsorption is largely mediated through the uptake of inorganic phosphate by Fe(III)-hydroxide (40, 41). In contrast, Enceladus's ocean water is overall reducing, carbonate-rich, and alkaline. In such ocean water, formation and persistence of Fe(III)-hydroxide is thermodynamically disfavored.

At alkaline pHs, green rust (another known scavenger of phosphate (42)) can form and metastably exist in the presence of reducing seawater with low Fe(III) content (43). However, green rust is not a thermodynamically stable phase and will eventually transform into greenalite (at high silica or low carbonate levels) or siderite (at low silica or high carbonate levels) (43–45). This transformation is more likely to occur in Enceladus's ocean given that its seafloor is likely to be 100s Ma to several Ga old (the relatively low derived density (2400 – 2500 kg/m^3) of its core (46) is consistent with the occurrence of abundant alteration phases, and argues against basaltic volcanism that would rejuvenate the seafloor). It can be expected that such long durations would support mineralogical transformations toward equilibrium (see **Section S1**). Moreover, the surface of green rust will become negatively charged at $pH > 8.3$ (47) (**Table S7**), which does not favor phosphate adsorption. Thus, adsorption onto $Fe(OH)_x$, including green rust, may not be a significant sink for P in Enceladus's ocean water.

Our geochemical model suggests favorable precipitation of carbonate minerals (calcite, magnesite, siderite, and dolomite) and phyllosilicates (lizardite, greenalite, talc, and tremolite) at Enceladus's seafloor. Surfaces of these minerals will be net negatively charged because their points of zero charge are lower than the inferred pH (8.5 - 11) of Enceladus ocean water (**Table S7**). Phosphate is negatively charged in Enceladus ocean water as well, mainly as HPO_4^{2-}. Thus, the electrostatic repulsion between negatively charged mineral surfaces and HPO_4^{2-} would result in minor uptake of phosphate by mineral adsorption, consistent with various experiments showing decreasing adsorption of phosphate at alkaline pHs (48–51). Moreover, dissolved (bi)carbonate in the Enceladus ocean would decrease phosphate adsorption onto secondary minerals (52). It is notable that at high concentrations of dissolved phosphate above the saturation limit of P-minerals, mineral adsorption might facilitate surface precipitation of P-minerals (53, 54). This effect is already captured by our model by assuming a P level that is in equilibrium with the least soluble P-mineral. Overall, mineral adsorption can be expected to have little if any influence on the present results.

S5. Impact of hydrothermal processes

The geochemical model presented in the main text is a low-temperature model. It is based on the high likelihood of there being an ice-covered (cold) ocean that is in contact with rocks on the ocean floor of Enceladus (55, 56). Low temperature water-rock interaction seems inescapable (8). The role of high temperature processes is less clear as the current observational evidence is indirect (4, 5), and we do not know how tidal heating is distributed between the ice shell and the rocky core (57, 58). Nevertheless, we are motivated to consider the impact of hydrothermal processes on the phosphate concentration in Enceladus's ocean because they could be important.

We construct a simple box model for phosphate in the Enceladus ocean. If there is heterogeneous heat generation or transfer in Enceladus's core, then there could be both low- and high-temperature fluids in the core. This would be similar to the situation at Earth's seafloor, where we can observe high-temperature venting at mid-ocean ridges and low-temperature off-axis fluid circulation (e.g., Campbell et al., 1988 (59); Wheat et al., 2017 (60)). Our box model assumes that low temperature dissolution of phosphate minerals is a source of phosphate to the ocean of Enceladus, while removal of phosphate-bearing ocean water into both low- and high-temperature systems in the rocky core are sinks (note that if high-temperature systems provide an additional source of phosphate, then there would be greater availability of phosphate in Enceladus's ocean than calculated below). The concentration of phosphate (*[P]*) in the ocean is related to the source and sinks by

$$\frac{d[\mathrm{P}]_{\mathrm{oc}}}{dt} = \frac{Q_{\mathrm{LT}}[\mathrm{P}]_{\mathrm{LT}} - Q_{\mathrm{LT}}[\mathrm{P}]_{\mathrm{oc}} - Q_{\mathrm{HT}}[\mathrm{P}]_{\mathrm{oc}}}{m_{\mathrm{oc}}}, \quad \text{(S2)}$$

where Q corresponds to the mass flow rate of water into/out of low temperature (LT) or high temperature (HT) systems in the core, and m_{oc} represents the mass of the ocean. Here, we consider an endmember in which it is assumed that phosphate is completely removed from the fluid during high-temperature circulation.

At steady state, the concentration of phosphate in the ocean will be

$$[\mathrm{P}]_{\mathrm{oc}} = \left(\frac{Q_{\mathrm{LT}}}{Q_{\mathrm{LT}} + Q_{\mathrm{HT}}}\right)[\mathrm{P}]_{\mathrm{LT}} = f_{\mathrm{LT}}[\mathrm{P}]_{\mathrm{LT}}. \quad \text{(S3)}$$

This equation shows that $[P]_{oc}$ should be some fraction of the phosphate concentration that is produced in the low temperature system. The latter was already estimated (e.g., **Fig. 2; S2, S4 & S5**). If hydrothermal processes are absent, then the equation collapses to the low temperature solution. When both low- and high-temperature fluid circulation occur, the challenge is to estimate the fraction of the total fluid flux between the ocean and core that is transported by low-temperature fluids only. An Earth analogy may help, in light of the lack of measurements of heat and fluid flow from Enceladus's core, and the likelihood (in our opinion) that these flows will be heterogeneous (not easy to calculate *a priori*) because geological systems are often complex. By extrapolating our knowledge of Earth's seafloor to Europa's, Lowell & DuBose (2005) (61) suggested that fluid circulation could transfer ~50% of the total heat flux, and high-temperature fluids would account for ~10-50% of the advective heat flux. While these numbers were for Europa, we note that Steel et al. (2017) (62) arrived at similar values (34 % and 30%, respectively) for Enceladus, based on the same general approach.

As a possible limiting case that maximizes the influences of hydrothermal processes on Enceladus, we consider a 50/50 partitioning between the amount of heat transferred by high temperature vs. low temperature fluids (calculating relative fluxes of fluids does not require heat flux magnitudes). Using an integrated equation for the relationship between the heat and mass flux (Eq. 34 in Glein et al., 2018 (63)), we find that f_{LT} in **Eq. (S3)** is larger than the corresponding heat flux fraction. This is because a larger quantity of low temperature fluid is required to transfer the same amount of heat as a high temperature fluid. The quantity f_{LT} is close to unity if the high temperature fluid is very hot (e.g., > 200 °C). It decreases as the two fluid temperatures begin to converge, but even at T_{HT} = 100 °C and T_{LT} = 25 °C, the value is still ~ 0.8. We conclude that the concentration of phosphate in the ocean will be determined by the low temperature source, unless fluid-mediated heat transfer on Enceladus is almost entirely dominated by high temperature fluids, which would be much different from what occurs on Earth.

S6. Comparison with previous thermodynamic model for Enceladus

The present geochemical model predicts much higher concentrations of dissolved phosphorus (up to 10^{-2} molal) in Enceladus's ocean than did an earlier model (less than 10^{-10} molal (64, 65). According to Zolotov (2012) (64), ß-whitlockite was the P-mineral that controlled the concentration of aqueous P in that model. We believe that our value for the dissolution equilibrium constant of ß-whitlockite in **Table S3** is representative and particularly relevant to the present problem, as it was pegged to the experimentally determined solubility product (K_{sp}) of $10^{-28.92}$ at 25 °C and 1 bar (66) (in our Enceladus model, there is a slight adjustment to 0 °C that is made using the van't Hoff equation). The solubility product quantifies the following equilibrium

$$Ca_3(PO_{4)2} \rightarrow 3Ca^{2+} + 2PO_4^{3-}. \qquad \text{(S4)}$$

The question is what is the solubility product from the earlier model? That model used the GEOCHEQ free energy minimization code (67) to determine water-rock equilibrium. We investigated ß-whitlockite solubility using a copy of the GEOCHEQ code that was given to C. Glein from M. Zolotov, when C. Glein worked at Arizona State University from 2006 – 2012. The GEOCHEQ value of the solubility product was calculated in two ways to verify internal consistency. First, we performed a numerical simulation in which a large amount of ß-whitlockite (1 kg) was reacted with pure water (1 kg) at 25 °C and 1 bar. The solubility product for **Reaction (S4)** can be computed using the equilibrium activities of Ca^{2+} and PO_4^{3-} via

$$K_{sp} = a^3_{Ca^{2+}} \times a^2_{PO_4^{3-}}. \qquad \text{(S5)}$$

Activity values from GEOCHEQ are $a\mathrm{Ca}^{2+} = 1.41 \times 10^{-8}$ and $a\mathrm{PO}_4^{3-} = 1.94 \times 10^{-14}$, yielding $\log K_{sp} = -50.98$. In a second approach, we calculated the solubility product using standard Gibbs free energy of formation values from the GEOCHEQ database. Those values are -952894 cal/mol for ß-whitlockite, -132120 cal/mol for the calcium cation, and -243500 cal/mol for the phosphate anion. We then computed the solubility product using the relationship

$$\Delta G^{\circ}_{Rxn\ S4} = -RT \times lnK_{sp}, \qquad \text{(S6)}$$

where R designates the gas constant (1.987 cal mol^{-1} K^{-1}). From this calculation, we obtained an almost identical $\log K_{sp}$ value of −50.97. It is evident that GEOCHEQ treats ß-whitlockite as being far less soluble than it should be based on mineral-solution equilibration experiments ($\log K_{sp} = -28.92$; (66)). This many orders of magnitude difference is the dominant reason why previous thermodynamic modeling of the Enceladus ocean predicted only trace availability of dissolved phosphorus. Indeed, **Fig. S10** shows that using the much more negative $\log K_{sp}$ derived from GEOCHEQ data would drastically lower the predicted P concentration in Enceladus's ocean from our modeling approach as well.

S7. Is biological synthesis the most plausible process to achieve a significant extent of phosphoanhydride bond formation in Enceladus's ocean?

To illustrate the thermodynamic potential to form phosphoanhydride (P-O-P) bonds under abiotic conditions, we consider the formation of adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and orthophosphate. This is the most important reaction that is used to transfer energy in life as we know it. The reaction can be represented by

$$ADP^{3-} + HPO_4^{2-} + H^+ \rightarrow ATP^{4-} + H_2O. \qquad \text{(S7)}$$

At modeled conditions for Enceladus's ocean (0 °C, 1 bar, pH ~8.5-11), HPO_4^{2-} will be the predominant form of orthophosphate (**Fig. 1**), and the fully deprotonated forms of ADP and ATP would be the predominant forms of these species. The pK_a values of the singly protonated forms, designated as $HADP^{2-}$ and $HATP^{3-}$, were calculated to be 7.26 and 7.66, respectively (68); these values are lower than the inferred ocean pH. Note that this approach neglects metal ion complexing of nucleotides, so it will provide a first-order estimate. The equilibrium constant for **Reaction (S7)** can be written as

$$K_{S7} = \frac{a_{ATP^{4-}} a_{H_2O}}{a_{ADP^{3-}} a_{HPO_4^{2-}} a_{H^+}} = \frac{a_{H_2O}}{a_{HPO_4^{2-}} a_{H^+}} \left(\frac{\gamma_{ATP^{4-}}}{\gamma_{ADP^{3-}}} \right) \left(\frac{m_{ATP^{4-}}}{m_{ADP^{3-}}} \right) = 1.8\,, \tag{S8}$$

where a_i stands for the activity of the *i*th species, γ_i denotes its activity coefficient, and m_i indicates the molal concentration of the species of interest. The value of the equilibrium constant at 0 °C and 1 bar was computed using the CHNOSZ package (69) with thermodynamic data from (68) and (70).

We can estimate the molar ratio of ATP^{4-}/ADP^{3-} at equilibrium by rearranging **Eq. (S8)**, if values are available for the other quantities in that equation. We obtained values for these quantities by performing aqueous speciation calculations using the SpecE8 app (thermo.com.V8.R6+ database) in The Geochemist's Workbench 2021 (similar to what ref. (8) did). Two cases of the major ion composition were considered: (1) a "salty" case with a chlorinity of 0.2 molal and a concentration of total carbonates of 0.1 molal; and (2) a "dilute" case with a chlorinity of 0.05 molal and a concentration of total carbonates of 0.01 molal (**Table S2**). By varying the concentration of orthophosphate and fixing the pH, we obtained values for the first term on the far right side of **Eq. (S8)**. The second term is more challenging to evaluate because ATP^{4-} and ADP^{3-} are not in the thermodynamic database that was used. Two approaches were taken to help bound the problem. In a first approach, we assumed that the ionic charge dominates the degree of non-ideal behavior of ATP^{4-} and ADP^{3-}, and treated $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ as proxies for them. The latter pyrophosphate species are in the thermodynamic database. Our second approach was simpler – we assumed that the activity coefficient ratio in **Eq. (S8)** can be approximated by unity. This may be reasonable if the rest of the nucleotide structure dominates their solution behavior, so that non-ideal effects tend to cancel out.

We find that the equilibrium concentrations of pyrophosphate species are much lower than those of orthophosphate species (**Fig. S13**), and ATP would also be many orders of magnitude lower in concentration than ADP (**Fig. S14**), if these species equilibrated under our modeled conditions for Enceladus's ocean, where a very conservative upper limit for [P] would be ~0.1 molal (**Fig. S8**). Comparison of **Figs. S13** and **S14** shows that the nature of the species that contains a phosphoanhydride bond has an important effect on exactly where the equilibrium lies. However, even for the more favorable case of pyrophosphate formation from a relatively high concentration (100 mmolal) of orthophosphate, the maximum equilibrium concentration of pyrophosphate species was computed to be no higher than ~30 µmolal. Although these are just two examples, our quantification is consistent with the common rule of thumb that it is difficult to form phosphoanhydride bonds in cold water. In general terms, the strongly unfavorable thermodynamic potential for the conversion of more than a miniscule amount of ADP to ATP in Enceladus's ocean implies that larger ratios of ATP/ADP (or analogous pairs of species) would require energy input that is directed in the forward direction of **Reaction (S7)**. Such constructive use of energy is a hallmark of life; thus, life would likely be implicated if this type of disequilibrium were found in samples from Enceladus's ocean.

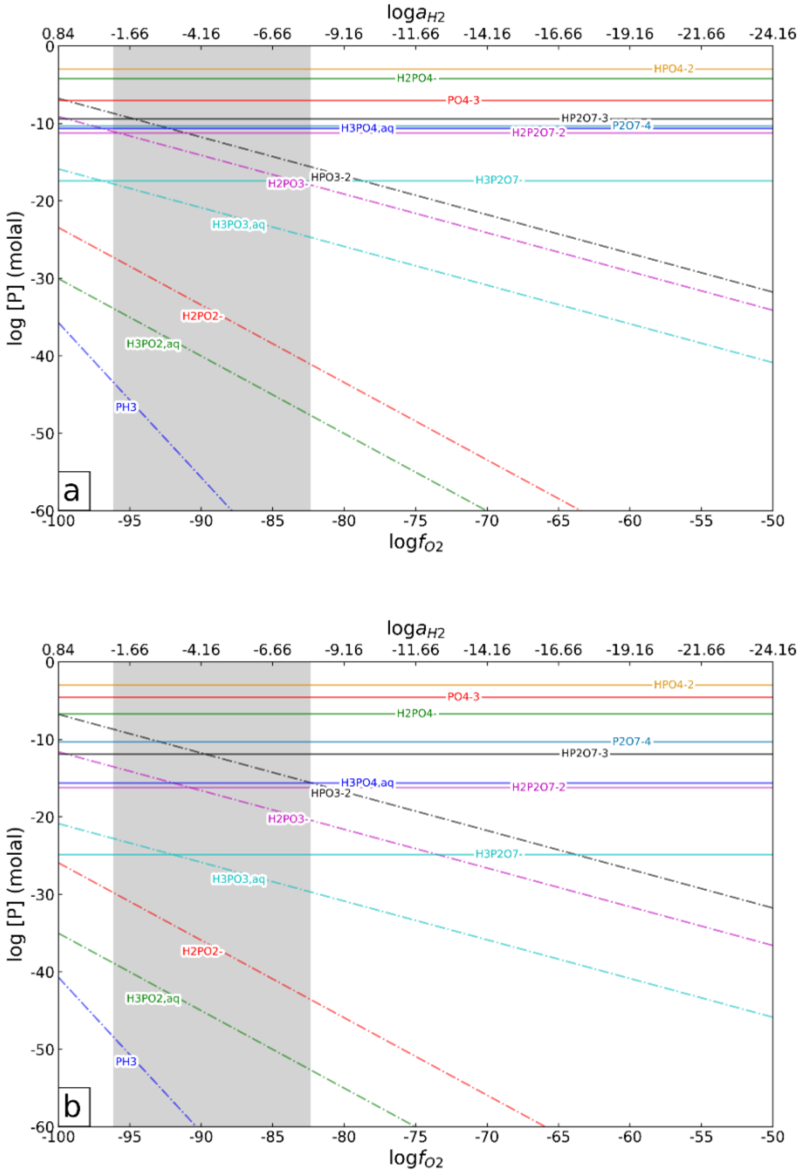

Fig. S1. Calculated equilibrium molal concentrations of aqueous P species as a function of ocean oxidation state (log $fO_{2,g}$; in bars) and pH for 1 mmolal total P at 0 °C and 70 bars, and (A) pH = 8.5 or (B) pH = 11, corresponding to the lower and upper ends of the constrained pH range of Enceladus ocean water, respectively. Thermodynamic properties for aqueous P species were compiled from the literature and are reported in **Table S1**. The shaded region represents inferred redox states of the Enceladus ocean: right limit calculated from $a(H_{2,aq})$ of Enceladus ocean water (63); left limit assuming $p(H_{2,g})$ equal to seafloor pressure (70 bars). Solid and dashed-dotted lines display levels of phosphates (+V) and reduced phosphorus (+III, +I, and -III), respectively.

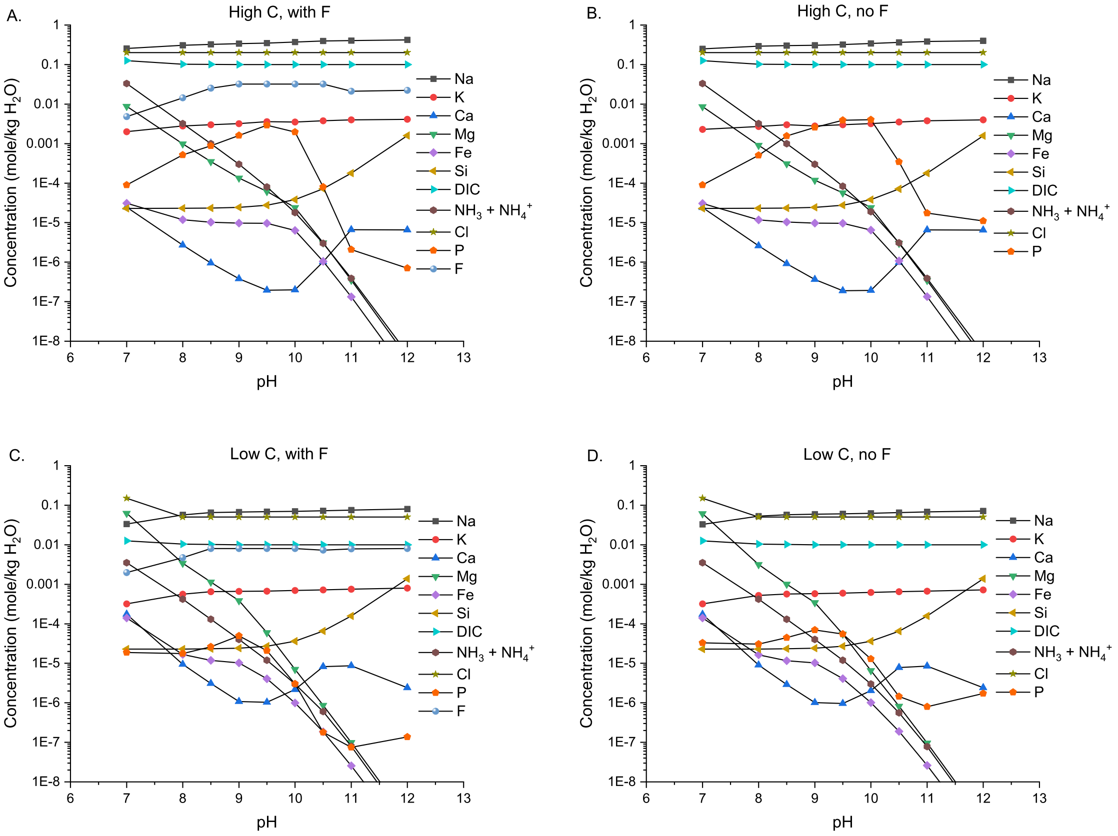

Fig. S2. Simulated equilibrium water chemistry under various nominal conditions of Enceladus's ocean (see **Table S2** for detailed settings) at 0 °C. DIC = Dissolved Inorganic Carbon (i.e., $CO_{2,aq}$ + HCO_3^- + CO_3^{2-}). [C] denotes the total concentration of carbonate ions: HCO_3^- + CO_3^{2-}. The system contains fluorine in the left panels, and fluorine is not included in the right panels.

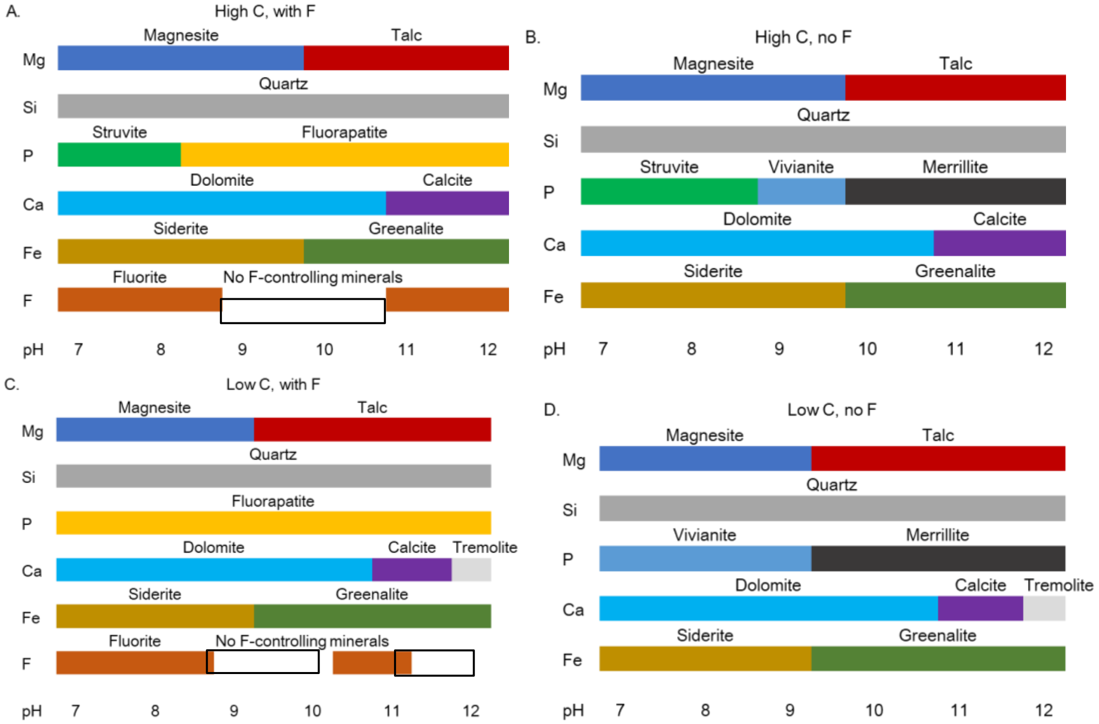

Fig. S3. Simulated saturated mineralogy on the seafloor under various nominal conditions of Enceladus's ocean (see **Table S2** for detailed settings) at 0 °C. [C] denotes the total concentration of carbonate ions: HCO_3^- + CO_3^{2-}. The system contains fluorine in the left panels, and fluorine is not included in the right panels.

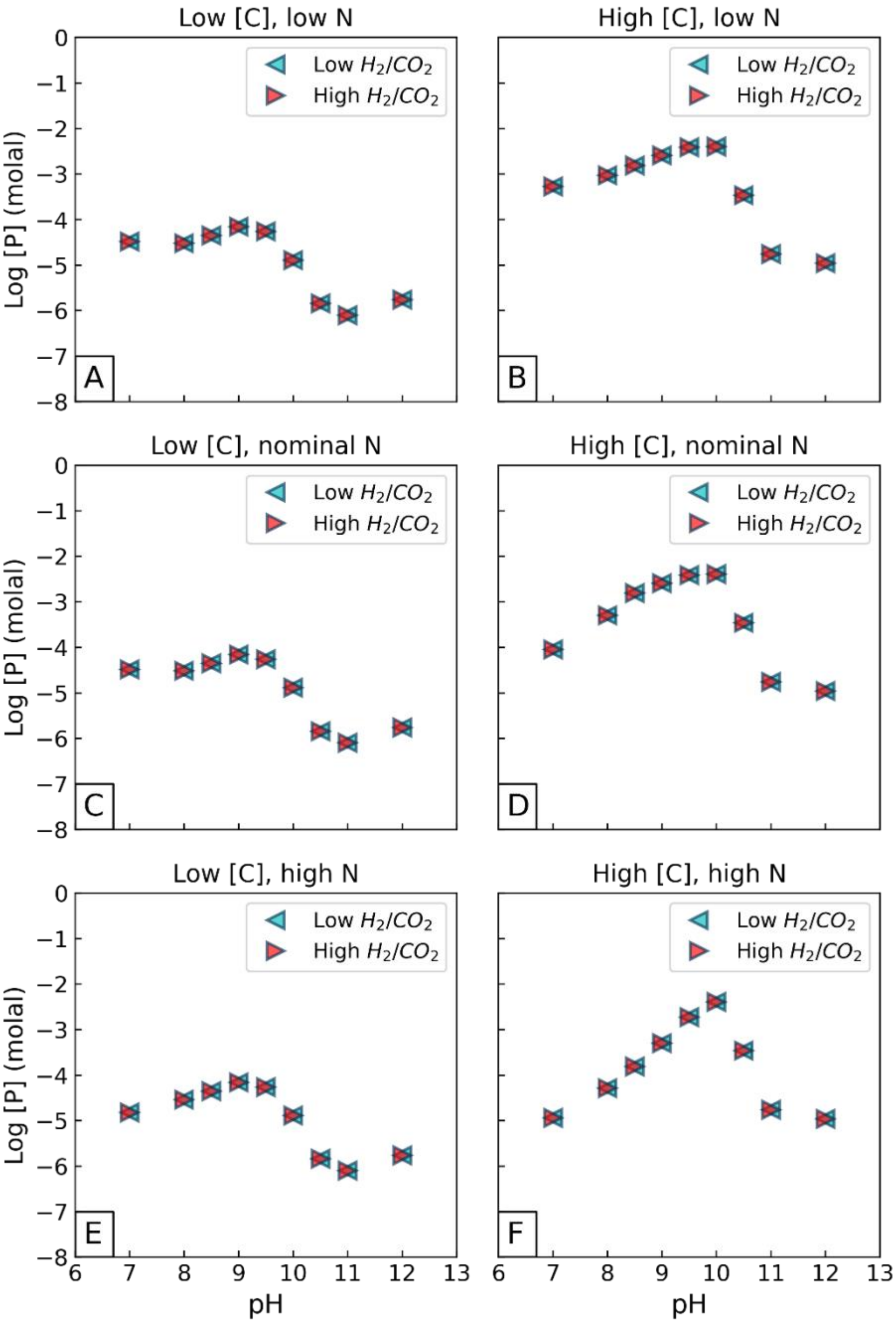

Fig. S4. Concentration of dissolved phosphate under various boundary conditions of Enceladus's ocean (see **Table S2** for detailed settings of A-F) at 0 °C. Fluorine is not included in this model. [C] denotes the total concentration of carbonate ions: HCO_3^- + CO_3^{2-}, [N] denotes the total concentration of $NH_{3,aq}$ and NH_4^+, and H_2/CO_2 denotes the concentration ratio of dissolved H_2 and CO_2.

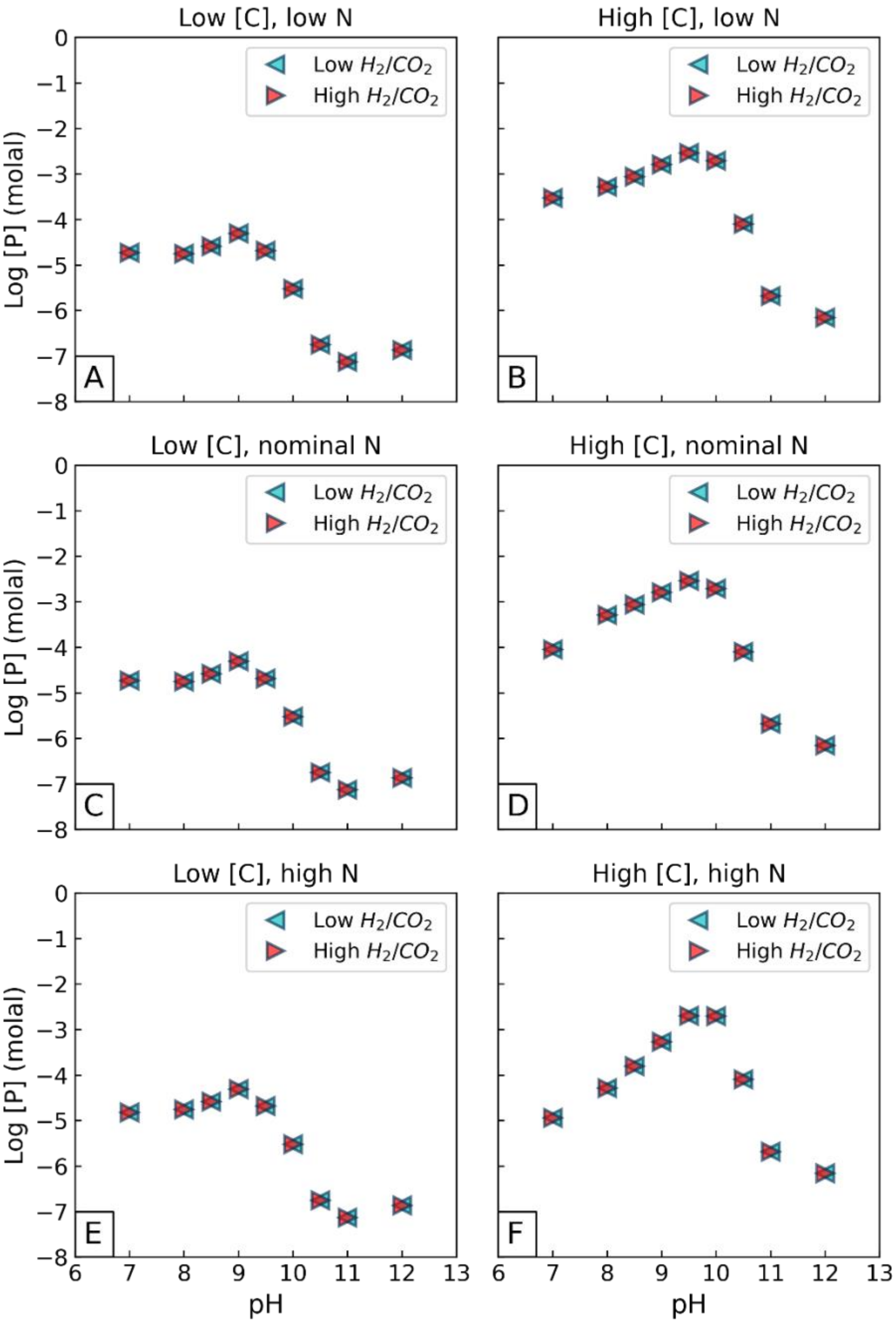

Fig. S5. Concentration of dissolved phosphate under various boundary conditions of Enceladus's ocean (see **Table S2** for detailed settings of A-F) at 0 °C. Fluorine is included in this model by assuming that its concentration is the lower value between the solubility of fluorite (the least soluble F-mineral in the system), and the abundance of F in Enceladus's ocean that would result from the ocean having a similar F/Cl ratio as CI chondrites (see **Section S1**). [C] denotes the total concentration of carbonate ions: $HCO_3^- + CO_3^{2-}$, [N] denotes the total concentration of $NH_{3,aq}$ and NH_4^+, and H_2/CO_2 denotes the concentration ratio of dissolved H_2 and CO_2.

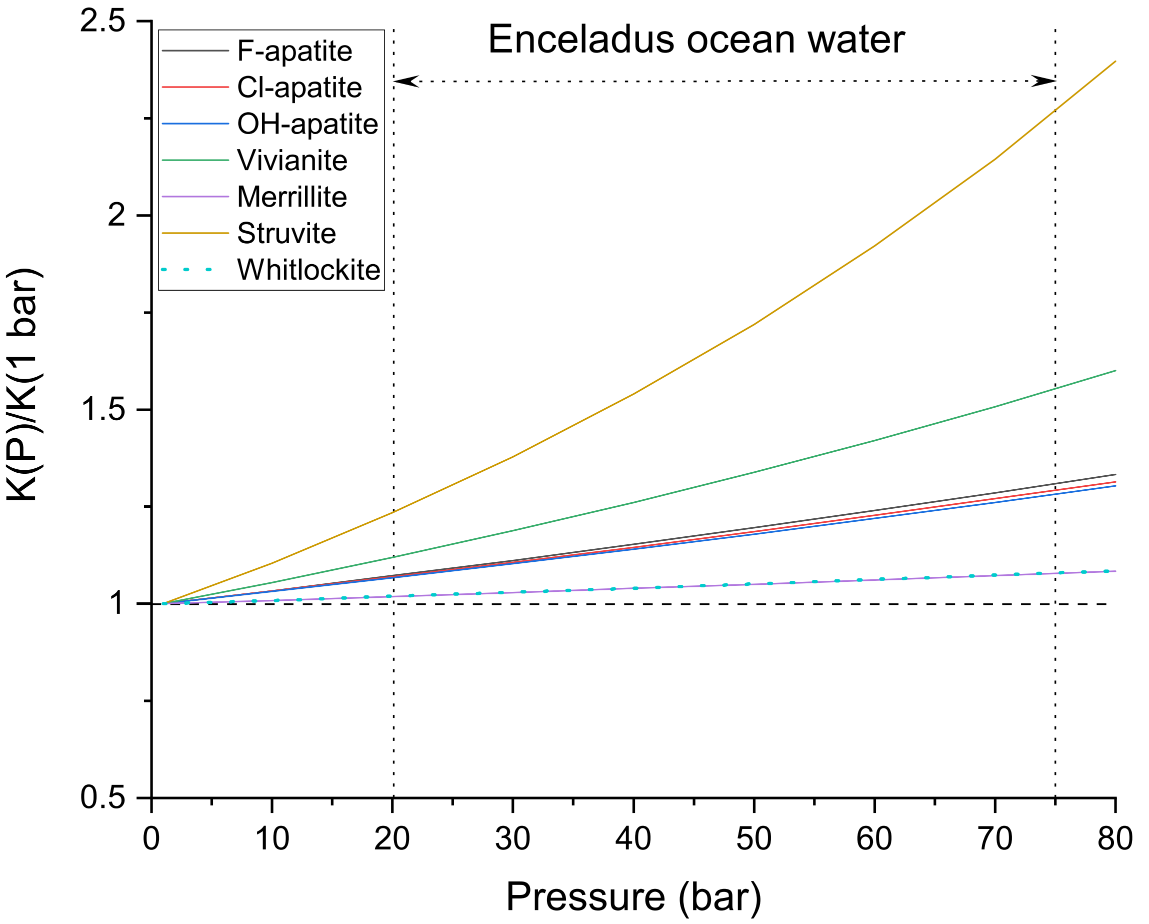

Fig. S6. Pressure effect on the solubilities of P-minerals. *K(P)* represents the equilibrium constant of dissolving a P-mineral to release 1 mole HPO_4^{2-} at different pressures. *K(P)/K(1 bar)* shows the ratio of equilibrium constant of reactions involving the noted minerals (per mole of HPO_4^{2-} formed) relative to the equilibrium constant at one bar, *K(1 bar)*. The horizontal dashed line shows where *K(P)/K(1 bar)* = 1: above this line, pressure produces a positive effect on the solubility and below this line, the solubility decreases with increasing pressure. Vertical dotted lines encompass the pressure range in Enceladus's ocean. Whitlockite is shown with a dotted curve to help distinguish it from merrillite.

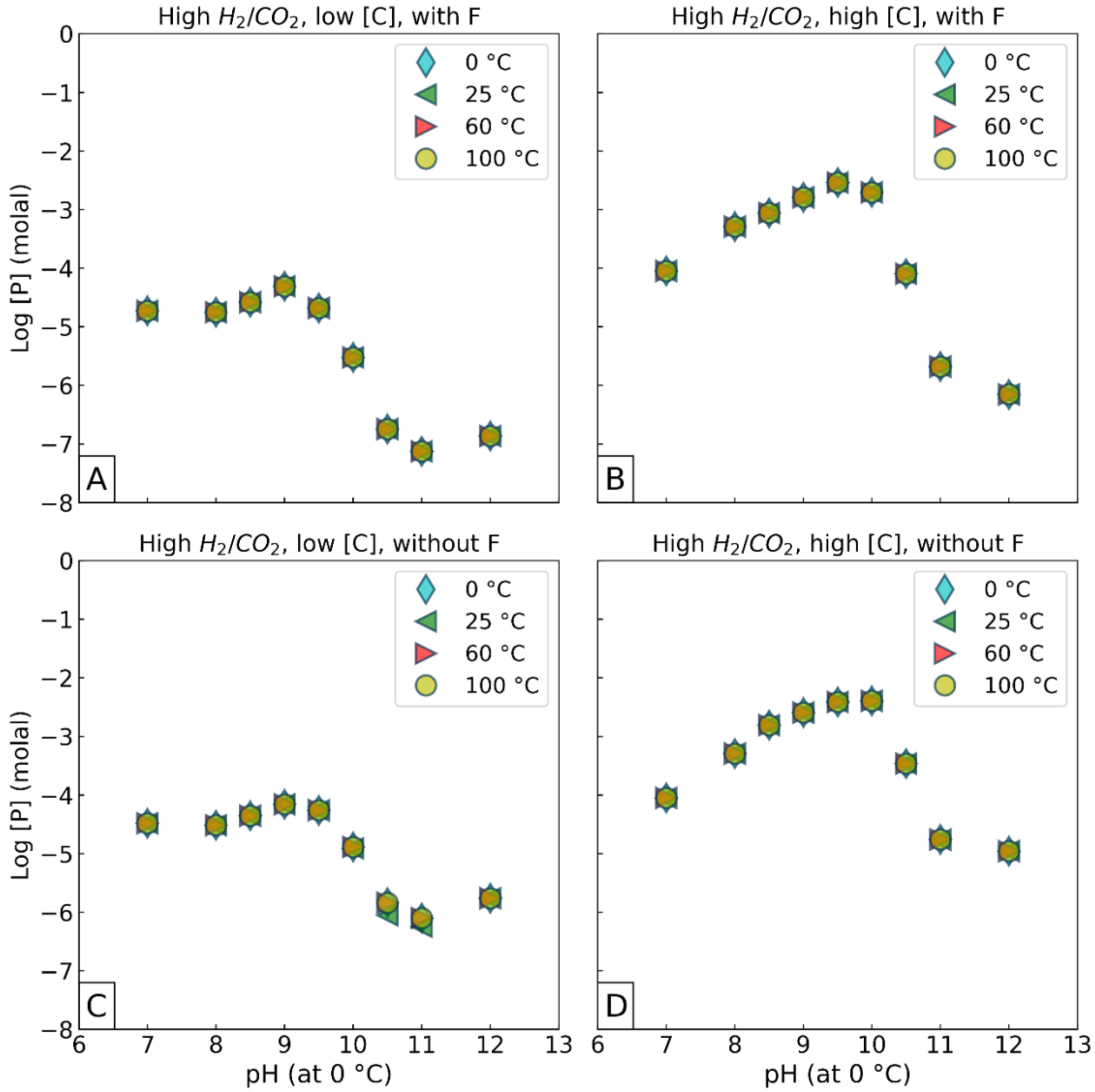

Fig. S7. Sensitivity tests of how heating of Enceladus ocean water affects dissolved phosphate levels. In these tests, the $(NH_3+NH_4^+)/CO_2$ molar ratio is assumed to be 1.5 (nominal condition). [C] denotes the total concentration of carbonate ions: HCO_3^- + CO_3^{2-}, and H_2/CO_2 denotes the concentration ratio of dissolved H_2 and CO_2. The system contains fluorine in the top panels, and fluorine is not included in the bottom panels.

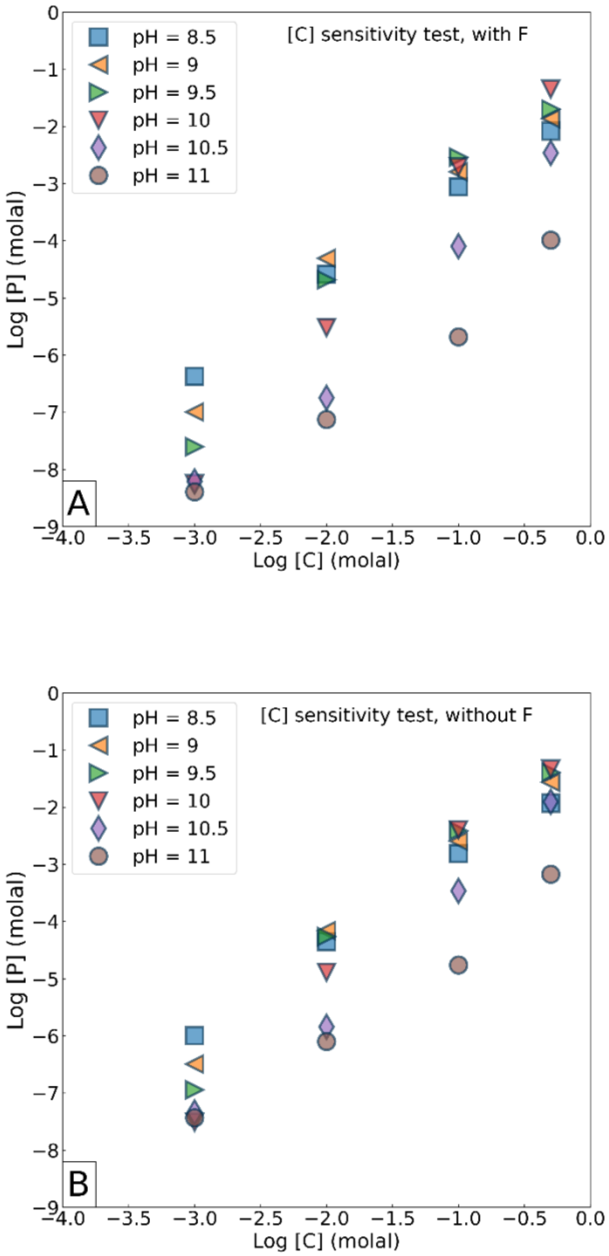

Fig. S8. Sensitivity tests of dissolved carbonate effects on dissolved phosphate levels at 0 °C. Here, it is assumed that the H_2/CO_2 molar ratio is 4.7 and the $(NH_3+NH_4^+)/CO_2$ molar ratio is 1.5 (nominal conditions). The system contains fluorine in the top panel, and fluorine is not included in the bottom panel.

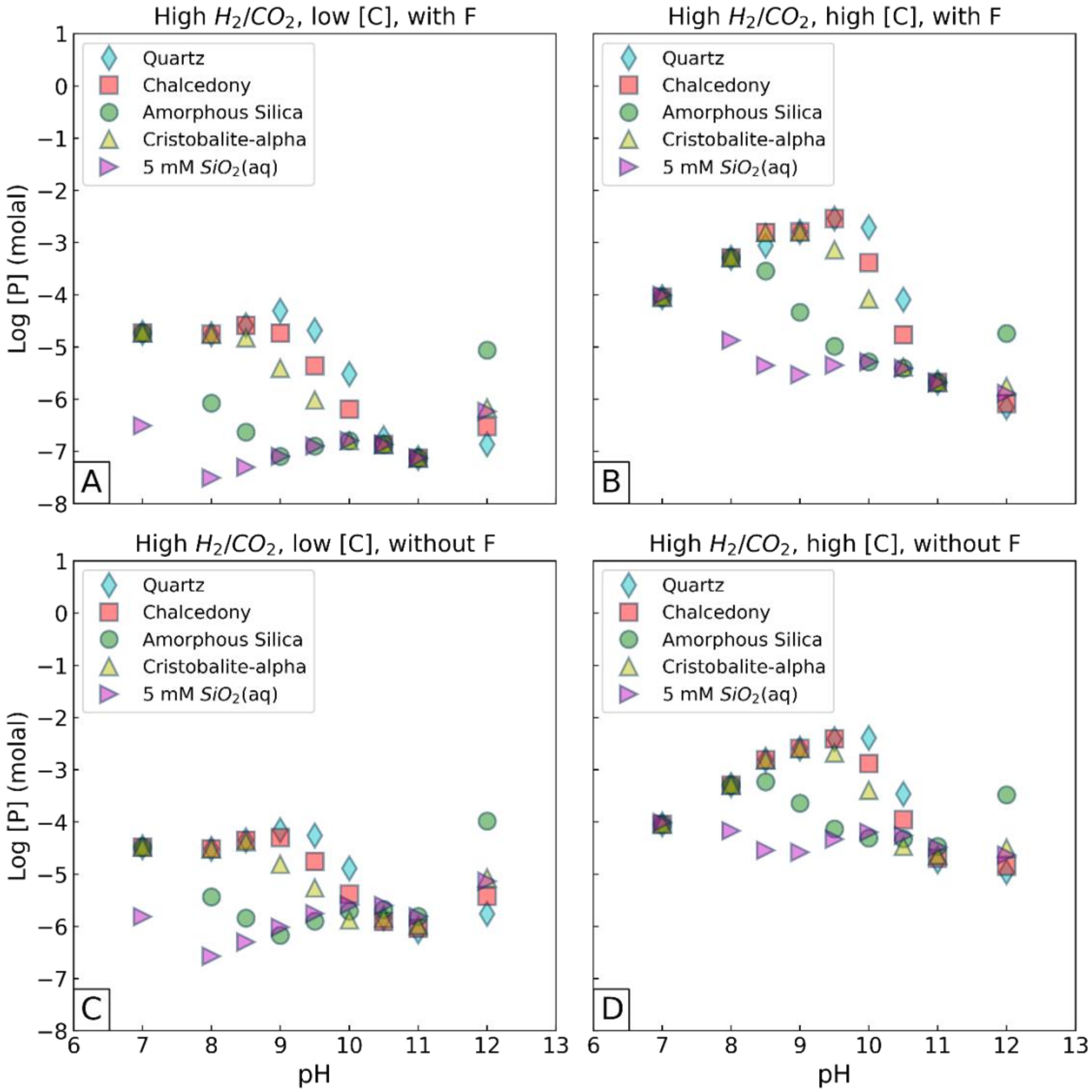

Fig. S9. Sensitivity tests showing how allowing various silica minerals to control the silica concentration as well as an arbitrarily high SiO_2(aq) concentration of 5 mM affect dissolved phosphate levels at 0 °C. The $(NH_3+NH_4^+)/CO_2$ molar ratio is assumed to be 1.5 (nominal condition). [C] denotes the total concentration of carbonate ions: HCO_3^- + CO_3^{2-}, and H_2/CO_2 denotes the concentration ratio of dissolved H_2 and CO_2. The system contains fluorine in the top panels, and fluorine is not included in the bottom panels.

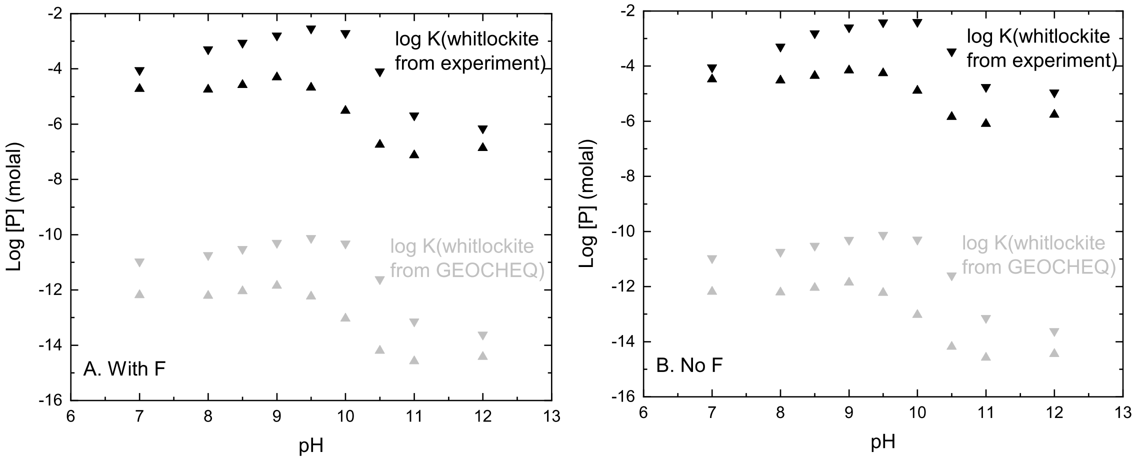

Fig. S10. Comparison of our predicted P concentrations in nominal model runs (**Table S2**; **Fig. 2**) with the results obtained by adopting log K_{sp} (for whitlockite) derived from GEOCHEQ thermodynamic data (64, 65). The system contains fluorine in the left panel, and fluorine is not included in the right panel.

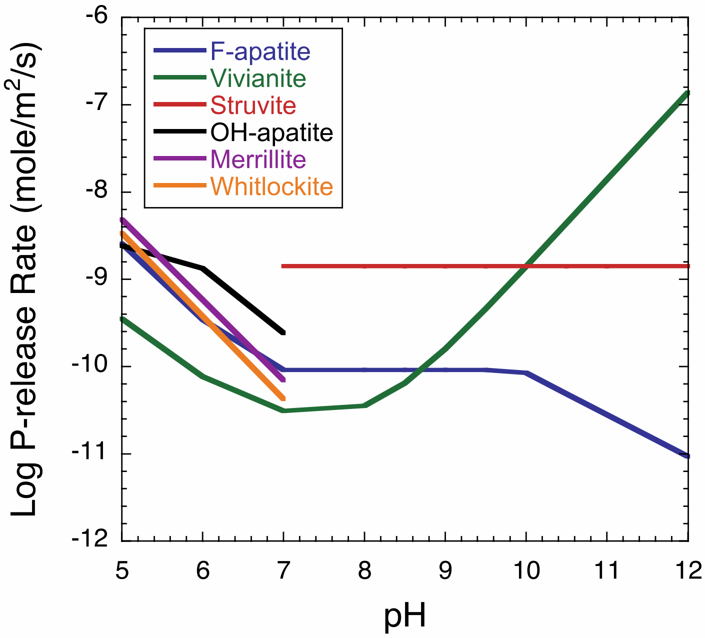

Fig. S11. Release rates of P from dissolution of common P-minerals under various pH conditions in previous studies at 25 °C. See **Table S5** for data sources.

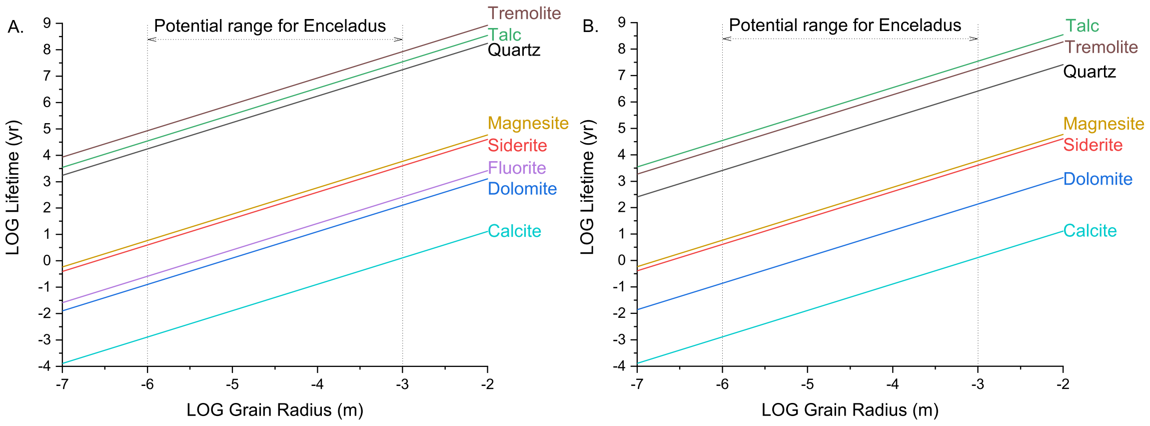

Fig. S12. Lifetime of mineral dissolution: A. pH = 8.5; B. pH = 11. Lifetime is defined as the duration for total dissolution of round crystals (71) at the given pH and 0 °C with kinetic dissolution rates for quartz (72), fluorite (73, 74), calcite (75), dolomite (72), magnesite (75), talc (76), tremolite (77), and siderite (72). Due to lack of kinetic data for fluorite dissolution at pH = 11, its lifetime could not be estimated at this pH.

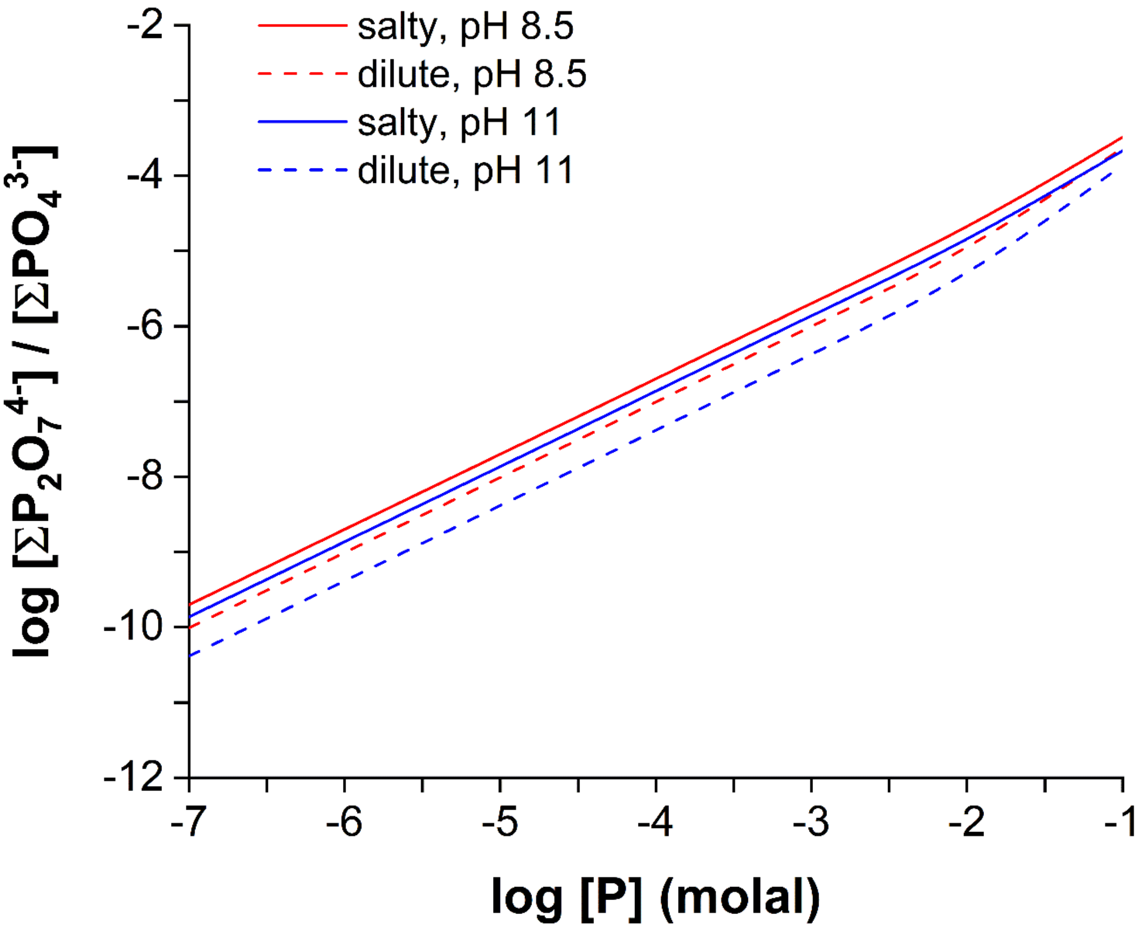

Fig. S13. Equilibrium concentration ratio of pyrophosphate species ($\Sigma P_2O_7^{4-} = P_2O_7^{4-} + HP_2O_7^{3-} + H_2P_2O_7^{2-} + H_3P_2O_7^{-} + H_4P_2O_{7,aq}$) to orthophosphate species ($\Sigma PO_4^{3-} = PO_4^{3-} + HPO_4^{2-} + H_2PO_4^{-} + H_3PO_{4,aq}$) as a function of the concentration of total phosphate and other geochemical conditions in Enceladus's ocean at 0 °C and 1 bar. Colored lines indicate the effects of pH over a previously inferred range, and solid vs. dashed lines show how the range of major salt concentrations (NaCl, $NaHCO_3/Na_2CO_3$; **Table S2**) affects the thermodynamic potential to produce pyrophosphate from orthophosphate.

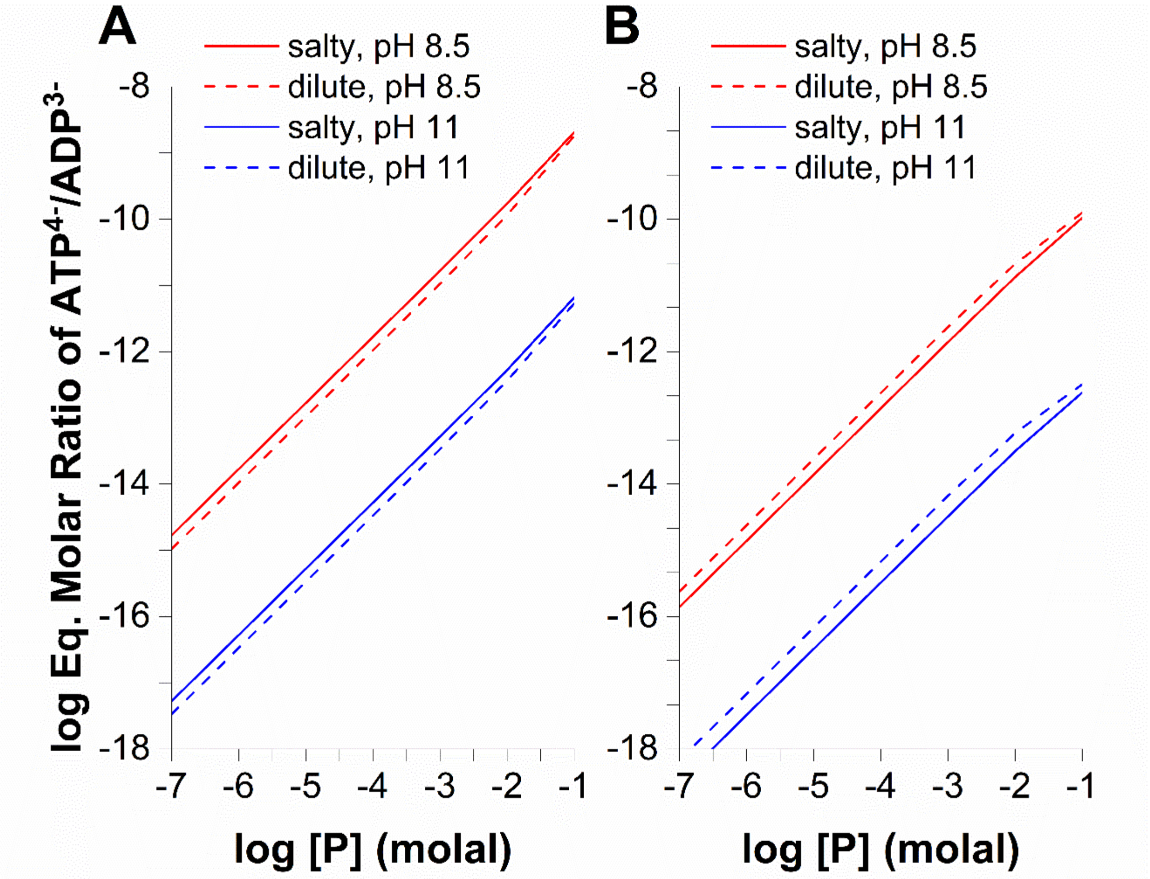

Fig. S14. Equilibrium molar ratio of adenosine triphosphate (ATP, fully deprotonated) to adenosine diphosphate (ADP, fully deprotonated) as a function of the concentration of total phosphate and other geochemical conditions in Enceladus's ocean at 0 °C and 1 bar. In (A), the activity coefficients of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ from speciation calculations (see **Section S7**) are used as proxies for those of ATP^{4-} and ADP^{3-}, respectively. In (B), the ATP^{4-}/ADP^{3-} activity coefficient ratio is assumed to be unity. Colored lines indicate the effects of pH over a previously inferred range, and solid vs. dashed lines show how the range of major salt concentrations (NaCl, $NaHCO_3/Na_2CO_3$; **Table S2**) affects the thermodynamic potential to produce ATP from ADP and orthophosphate.

Table S1. Thermodynamic properties of aqueous phosphorus species used in the Deep Earth Water (DEW) model to generate the equilibrium speciation diagram (**Fig. 1**).

Species		$\Delta G_f^{\circ\,a,f}$	$\Delta H_f^{\circ\,b,f}$	$S^{o\ c,f}$	$V^{o\ d,f}$	$C_p^{o\ e,f}$	$a_1 \times 10$	$a_2 \times 10^{-2}$	a_3	$a_4 \times 10^{-4}$	c_1	$c_2 \times 10^{-4}$	$\omega \times 10^{-5}$
Formula	Valence	cal mol^{-1}	cal mol^{-1}	cal mol^{-1} K^{-1}	cm^3 mol^{-1}	cal mol^{-1} K^{-1}	cal mol^{-1} bar^{-1}	cal mol^{-1}	cal K mol^{-1} bar^{-1}	cal K mol^{-1}	cal mol^{-1} K^{-1}	cal K mol^{-1}	cal mol^{-1}
$PH_{3,aq}$	-III	6060	-2680	27.4	24.4	50.5	6.2	1.6	3.5	-2.8	33.9	7.3	-0.2
$H_3PO_{2(aq)}$	+I	-125100	-145600	36.9	35.4	14.1	8.3	3.6	1.8	-2.9	12.4	-0.2	-0.2
$H_2PO_2^-$	+I	-122400	-146700	24.1	22.0	-7.0	6.4	1.8	3.3	-2.9	13.7	-4.5	1.3
$H_3PO_{3(aq)}$	+III	-204800	-230600	43.6	19.1	25.1	5.1	0.5	4.4	-2.8	17.9	2.1	-0.3
$H_2PO_3^-$	+III	-202350	-231700	31.7	14.7	5.5	4.9	0.4	4.5	-2.8	20.0	-1.9	1.1
HPO_3^{2-}	+III	-194000	-231600	4.0	4.5	-40.2	3.9	-0.6	5.3	-2.8	11.7	-11.2	3.2
$H_3PO_{4(aq)}$	+V	-273100	-307920	38.0	48.1	23.6	10.8	6.0	-0.2	-3.0	18.0	1.8	-0.2
$H_2PO_4^-$	+V	-270140	-309820	21.6	31.3	-7.0	8.2	3.5	1.9	-2.9	14.0	-4.5	1.3
HPO_4^{2-}	+V	-260310	-308815	-8.0	5.4	-58.3	4.2	-0.3	5.1	-2.8	2.7	-14.9	3.3
PO_4^{3-}	+V	-243500	-305300	-53.0	-30.6	-124.6	-1.2	-7.3	9.6	-2.5	-15.2	-28.4	5.6
$P_2O_7^{4-}$	+V	-458700	-542800	-28.0	21.7	-139.1	7.1	9.5	2.0	-3.2	-11.7	-31.4	6.9
$HP_2O_7^{3-}$	+V	-471400	-543700.	11.0	36.5	-28.7	8.3	12.6	0.8	-3.3	32.2	-8.9	4.6
$H_2P_2O_7^{2-}$	+V	-480400	-544600	39.0	47.1	17.6	9.1	14.4	0.1	-3.4	40.6	0.6	2.6

[a]Standard Gibbs free energy of formation at 25 °C and 1 bar; [b]standard enthalpy of formation; [c]standard partial molal entropy; [d]standard partial molal volume; [e]standard partial molal heat capacity; [f]thermodynamic properties (G, H, S, V, C_p) of $PH_{3,aq}$ come from Schulte et al. (2001) (78) and other species from Shock et al. (1997) (70), with a_1-a_4, c_1-c_2 and ω parameters for the revised Helgeson-Kirkham-Flowers equations of state that are estimated using the DEW methodology (Sverjensky et al., 2014) (79).

Table S2. Model assumptions for Enceladus ocean water chemistry simulations.

Element	**Basis for assumption**
Na	Charge balance (1, 63)
K	0.01 × c(Na^+) (1, 63)
Cl[a]	0.2 molal at high $CO_{2,aq}$ case; 0.05 molal at low $CO_{2,aq}$ case (1, 63)
Ca	Minimum solubility of secondary Ca-minerals (e.g., dolomite, calcite, aragonite, or tremolite)
F	Lower value between solubility of fluorite or $(F/Cl)_{solar}$ × c(Cl^- in Enceladus ocean water) in the case of F-presence
Mg	Minimum solubility of secondary Mg-minerals (e.g., magnesite, talc)
Fe	Minimum solubility of secondary Fe-minerals (e.g. siderite, greenalite, goethite, hematite, magnetite)
Si	Minimum solubility of quartz, chalcedony, cristobalite, or amorphous silica
P	Minimum solubility of P-minerals (e.g., apatite, vivianite, struvite, merrillite, etc., see **Table S3**)
Total carbonate species[b]	0.1 molal for high C case; 0.01 molal for low C case (1, 63)
$H_{2,aq}$[c]	$H_{2,aq}/CO_{2,aq}$ = 4.7 for high H_2 case; $H_{2,aq}/CO_{2,aq}$ = 0.5 for low H_2 case (4, 63)
Total ammonia[d]	$\Sigma NH_3/CO_{2,aq}$ = 0.15, 1.5, or 15, representing low, nominal, or high N case. Nominal value (1.5) is taken directly from plume gas data (4).

[a] Based on the observational constraint being the carbonates/chloride ratio, and the fact that the concentration of CO_2 increases with an increase in total carbonates concentration at fixed pH; [b] total carbonate species = [CO_3^{2-}] + [HCO_3^-]; [c] H_2 activity estimated here should represent an upper bound due to the condensation of $CO_{2,g}$ of unknown extent at the surface of the tiger stripe fractures. This effect is expected to increase the molar ratio of H_2/CO_2 in the plume gas relative to the ocean (80). [d] The high N case could be representative of the ocean if NH_3 undergoes significant freeze out from the plume gas relative to CO_2. A low N case is also considered in case some NH_3 that was detected by INMS was non-native to the plume and produced by thermally induced decomposition of N-bearing organics inside INMS (81). At least some native plume NH_3 is indicated by the independent detection of plume-derived nitrogen ions in Saturn's inner magnetosphere by the Cassini Plasma Spectrometer (82).

Table S3. Aqueous phosphate species and phosphate minerals included in the EQ3 database.

Aqueous species	$H_3PO_{4,aq}$; $H_2PO_4^-$; HPO_4^{2-}; PO_4^{3-}; $H_2P_2O_7^{2-}$; $HP_2O_7^{3-}$; $P_2O_7^{4-}$; $CaH_2PO_4^+$; $CaHPO_{4,aq}$; $CaPO_4^-$; $Fe(II)H_2PO_4^+$; $Fe(III)H_2PO_4^{2+}$; $Fe(II)HPO_{4,aq}$; $Fe(III)HPO_4^+$; $MgHPO_{4,aq}$; $MgH_2PO_4^+$; $Mg(HPO_4)_2^{2-}$; $MgPO_4^-$; $NaPO_4^{2-}$; $Na_2PO_4^-$; $NaHPO_4^-$; $Na_2HPO_{4,aq}$

Mineral	Chemical formula	Dissolution reaction	Log K[a]	ΔH_r[a] (kJ/mole)
Fluorapatite	$Ca_5(PO_4)_3F$	$Ca_5(PO_4)_3F + 3H^+ \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + F^-$	-22.8[b]	-104[b]
Hydroxylapatite	$Ca_5(PO_4)_3OH$	$Ca_5(PO_4)_3OH + 4H^+ \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + H_2O$	-5.11[b]	-183[b]
Chlorapatite	$Ca_5(PO_4)_3Cl$	$Ca_5(PO_4)_3Cl + 3H^+ \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + Cl^-$	-9.60[b]	-161[b]
ß-Whitlockite	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2 + 2H^+ \rightarrow 3Ca^{2+} + 2HPO_4^{2-}$	-4.28[c]	-84.6[c]
Whitlockite	$Ca_9Mg(HPO_4)(PO_4)_6$	$Ca_9Mg(HPO_4)(PO_4)_6 + 6H^+ \rightarrow 9Ca^{2+} + Mg^{2+} + 7HPO_4^{2-}$	-39[d]	-393[e]
Merrillite	$Ca_{9.5}Mg(PO_4)_7$	$Ca_{9.5}Mg(PO_4)_7 + 7H^+ \rightarrow 9.5Ca^{2+} + Mg^{2+} + 7HPO_4^{2-}$	-39[d]	-401[e]
Calcium hydrogen phosphate	$CaHPO_4$	$CaHPO_4 \rightarrow Ca^{2+} + HPO_4^{2-}$	-6.9[f]	-17.2[f]
Vivianite	$Fe_3(PO_4)_2{\cdot}8H_2O$	$Fe_3(PO_4)_2{\cdot}8H_2O + 2H^+ \rightarrow 3Fe^{2+} + 2HPO_4^{2-} + 8H_2O$	-11.1[g]	-24.3[g]
Newberyite	$MgHPO_4{\cdot}3H_2O$	$MgHPO_4{\cdot}3H_2O \rightarrow Mg^{2+} + HPO_4^{2-} + 3H_2O$	-5.83[h]	-27.9[e]
Bobierrite	$Mg_3(PO_4)_2{\cdot}8H_2O$	$Mg_3(PO_4)_2{\cdot}8H_2O + 2H^+ \rightarrow 3Mg^{2+} + 2HPO_4^{2-} + 8H_2O$	-0.51[i]	-69.3[e]
K-struvite	$KMgPO_4{\cdot}6H_2O$	$KMgPO_4{\cdot}6H_2O + H^+ \rightarrow K^+ + Mg^{2+} + HPO_4^{2-} + 6H_2O$	1.73[i]	-0.89[j]
Na-struvite	$NaMgPO_4{\cdot}7H_2O$	$NaMgPO_4{\cdot}7H_2O + H^+ \rightarrow Na^+ + Mg^{2+} + HPO_4^{2-} + 7H_2O$	0.76[k]	11.5[e]
Brushite	$Ca(HPO_4){\cdot}2H_2O$	$Ca(HPO_4){\cdot}2H_2O \rightarrow Ca^{2+} + HPO_4^{2-} + 2H_2O$	-6.56[l]	0.17[l]
Octacalcium phosphate	$Ca_4H(PO_4)_3{\cdot}2.5H_2O$	$Ca_4H(PO_4)_3{\cdot}2.5H_2O + 2H^+ \rightarrow 4Ca^{2+} + 3HPO_4^{2-} + 2.5H_2O$	-11.3[m]	-123[e]
Struvite	$NH_4MgPO_4{\cdot}6H_2O$	$NH_4MgPO_4{\cdot}6H_2O + H^+ \rightarrow Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O$	-13.4[n]	84.0[n]
Strengite	$Fe(PO_4){\cdot}2H_2O$	$Fe(PO_4){\cdot}2H_2O + H^+ \rightarrow Fe^{3+} + HPO_4^{2-} + 2H_2O$	-14.1[o]	-24.3[p]
Francolite	$Ca_{10}(PO_4)_{5.5}(CO_3)_{0.5}F_{2.5}$	$Ca_{10}(PO_4)_{5.5}(CO_3)_{0.5}F_{2.5} + 5.5H^+ \rightarrow 10Ca^{2+} + 5.5HPO_4^{2-} + 0.5CO_3^{2-} + 2.5F^-$	-23.3[q]	No data

[a] Data at 25 °C and 1 bar; [b] calculated by SUPCRT92b with $\Delta G_{f,mineral}$ from Zhu & Sverjensky (1991)(24); [c] Gregory et al. (1974) (66); [d] Adcock et al. (2013)(83); [e] calculated using $\Delta H_{f,mineral}$ that was estimated by the method proposed in Iglesia (2009)(84); [f] McDowell et al. (1971)(85); [g] Al-Borno & Tomson (1994)(86); [h] Racz & Soper (1968)(87); [i] Taylor et al. (1963)(88); [j] Luff & Reed (1980)(89); [k] Xu et al. (2015)(90); [l] Patel et al. (1974)(91); [m] Tung et al. (1988)(92); [n] Bhuiyan et al. (2007)(93); [o] Nriagu (1972)(94); [p] Egan et al. (1961)(95); [q] Vieillard (1978)(96).

Table S4. Comparison of equilibrium minerals in our simulations and minerals in chondrites that were altered by aqueous fluids. Note that we made the common approximation in geochemical modeling of treating minerals as pure endmembers, while chondritic minerals often exist as more complex solid solutions.

Element	Mineral	Chemical formula	This study	Chondrites[a]
Si	Quartz	SiO_2	√	√
F	Fluorite	CaF_2	√	√
Ca	Calcite	$CaCO_3$	√	√
	Dolomite	$CaMg(CO_3)_2$	√	√
Mg	Magnesite	$MgCO_3$	√	√
	Talc	$Mg_3Si_4O_{10}(OH)_2$	√	√
	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	√	√
Fe	Siderite	$FeCO_3$	√	√
	Greenalite	$Fe_3Si_2O_5(OH)_4$	√	√
P	Apatite	$Ca_5(PO_4)_3(OH,Cl,F)$	√	√
	Merrillite	$Ca_{9.5}Mg(PO_4)_7$	√	√
	Vivianite	$Fe_3(PO_4)_2*8H_2O$	√	√
	Struvite	$MgNH_4PO_4*6H_2O$	√	(√)[b]

[a] Observed as secondary minerals produced by aqueous alteration (6, 97–100); [b] Likely to be present but not observed in chondrites probably due to how easily struvite can be converted to other phosphates (via loss of ammonium in low-N aqueous solutions, or thermal decomposition to form Mg-phosphate or Ca-phosphate at elevated temperatures) (101).

Table S5. Dissolution kinetics of phosphate minerals.

Mineral	Chemical formula	Molar mass (g/mole)	Density (g/cm^3)[a]	pH	Dissolution rate (mole/m^2/s)[b]	Activation energy (kJ/mole)	Reference(s)
F-apatite	$Ca_5(PO_4)_3F$	504.3	3.2	3-7 7-10 > 10	log R = -0.87 × pH - 5.0 Constant (-10.8) log R = -0.48 × pH - 6.1	46	Chairat et al. (2007) (102); Harouiya et al. (2007) (103)
OH-apatite	$Ca_5(PO_4)_3(OH)$	502.3	3.2	< 7	$R = -8.9 \times 10^{-10} \times \frac{9.96 \times 10^5 \times a_{H^+}}{1 + 9.96 \times 10^5 \times a_{H^+}}$	No data	Oliva et al. (2012) (104)
Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$	501.6	2.7	2-10	$R = 1.18 \times 10^{-10} a_{H^+}^{0.77} + 1 \times 10^{-15} + 6.92 \times 10^{-24} a_{H^+}^{-1}$	No data	Thinnappan et al. (2008) (105)
Merrillite	$Ca_{9.5}Mg(PO_4)_7$	1070	3.1	2-5	log R = -0.92 × pH – 4.56	No data	Adcock et al. (2013) (83)
Struvite	$MgNH_4PO_4 \cdot 6H_2O$	245.4	1.7	7-11	Constant (-8.85)	44.8	Roncal-Herrero & Oelkers (2011) (32); Babić-Ivančić et al. (2002)(106)
Whitlockite	$Ca_9Mg(HPO_4)(PO_4)_6$	1051	3.1	2-5	log R = -0.95 × pH -4.50	No data	Adcock et al. (2013) (83)

[a]Density from mindat.org; [b]Kinetic experiment at 25 °C except vivianite (18.5 °C).

Table S6. Calculated abundances of elements in Enceladus's ocean based on model assumptions.

Element	CI chondrites[a]	Molecular weight	c (max from rock)[b]	c(pH = 8.5)[c]		c(pH = 11)[c]	
	ppm (ug/g)	g/mole	mole/kg H_2O	High Carbonate[d]	Low Carbonate[e]	High Carbonate[f]	Low Carbonate[g]
C	35180	12.011	1.03E+01	1.00E-01	1.02E-02	1.00E-01	1.00E-02
N	2940	14.007	7.35E-01	1.00E-03	1.30E-04	3.90E-07	8.00E-08
F	60.6	18.998	1.12E-02	2.53E-02	8.00E-03	2.10E-02	7.84E-03
Na	5010	22.99	7.63E-01	3.25E-01	6.52E-02	4.04E-01	7.56E-02
Mg	95870	24.305	1.38E+01	3.51E-04	1.14E-03	3.51E-07	9.95E-08
Si	106500	28.085	1.33E+01	2.33E-05	2.33E-05	1.79E-04	1.58E-04
P	920	30.974	1.04E-01	8.80E-04	2.61E-05	2.08E-06	7.49E-08
Cl	704	35.45	6.95E-02	2.00E-01	5.00E-02	2.00E-01	5.00E-02
K	530	39.098	4.74E-02	3.25E-03	6.50E-04	4.04E-03	7.50E-04
Ca	9070	40.078	7.92E-01	9.50E-07	3.10E-06	6.63E-06	8.71E-06
Fe	182800	55.845	1.15E+01	1.03E-05	1.18E-05	1.32E-07	2.54E-08

[a] Average abundances of elements in CI chondrites (19); [b] concentration of elements assuming total dissolution from Enceladus's core (7×10^{19} kg rock) into the global ocean (2×10^{19} kg water); [c] concentration of elements (mole/kg H_2O) in our nominal model runs (N/CO_2 molar ratio = 1.5) at 0 °C and with F as an example (see **Fig. S2** for more results in graphical form); [d] equilibrium minerals present (**Fig. S3A**): magnesite, dolomite, siderite, fluorite, quartz, F-apatite, struvite (close to saturation), chalcedony (close to saturation); [e] equilibrium minerals present (**Fig. S3C**): magnesite, dolomite, siderite, fluorite, quartz, F-apatite, chalcedony (close to saturation); [f] equilibrium minerals present (**Fig. S3A**): talc, calcite, greenalite, fluorite, quartz, F-apatite, aragonite (close to saturation), chalcedony (close to saturation), dolomite (close to saturation); [g] equilibrium minerals present (**Fig. S3C**): talc, calcite, greenalite, fluorite, quartz, F-apatite, aragonite (close to saturation), chalcedony (close to saturation).

Table S7. pH of the point of zero charge (pH_{pzc}) of minerals. In Enceladus ocean water (estimated pH between 8.5 and 11), all of the listed minerals would have net negatively charged surfaces.

Mineral name	Formula	pH_{pzc}	Data source
Ferrihydrite	$Fe_{10}O_{14}(OH)_2$	8	Hiemstra (2013) (107)
Green rust	$Fe_6(OH)_{12}(CO_3,SO_4)$	8.3	Guilbaud et al. (2013) (47)
Calcite	$CaCO_3$	8	Santos et al. (2015) (108)
Siderite	$FeCO_3$	5.3	Charlet et al. (1990) (109)
Magnesite	$MgCO_3$	6.7	Chen & Tao (2005) (110)
Dolomite	$CaMg(CO_3)_2$	6.3	Chen & Tao (2005) (110)
Quartz	SiO_2	3	Sverjensky & Sahai (1996) (111)
Amorphous silica	$SiO_2 * nH_2O$	2.8	Sverjensky (2006) (112)
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	6.7	Sverjensky & Sahai (1996) (111)
Talc	$Mg_3Si_4O_{10}(OH)_2$	6.7	Sverjensky & Sahai (1996) (111)
Lizardite	$Mg_3Si_2O_5(OH)_4$	4.3	Alvarez-Silva et al. (2010) (113)
Vivianite	$Fe_3(PO_4)_2 * 8H_2O$	5.3	Thinnappan et al. (2008) (105)
OH-apatite	$Ca_5(PO_4)_3(OH)$	8.5	Bell et al. (1973) (114)
F-apatite	$Ca_5(PO_4)_3F$	6.7	Bell et al. (1973) (114)
Fluorite	CaF_2	8.2	Jiang et al. (2018) (115)

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