PNAS
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Supplementary Information for

A carbonate-rich lake solution to the phosphate problem of the origin of life

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This PDF file includes:

www.pnas.org/cgi/doi/10.1073/pnas.1916109117

Supplementary Material

Appendix A: The composition of carbonate-rich lakes

Carbonate-rich lakes accumulate a number of ions, in addition to phosphate, from their hydrologic basins, and concentrate these ions until they precipitate from solution as salts (1) (Fig. S1). Most ion concentrations in carbonate-rich lakes, with the exception of Ca^{2+} and Mg^{2+}, increase linearly with phosphate in approximately 1:1 trends (Fig. S1). This indicates that phosphate in carbonate-rich lakes behaves as a conservative solute, that is, it does not precipitate during evaporation as a salt. This is in stark contrast to the situation in most surface waters on Earth, where phosphate has a highly non-conservative behavior and precipitates as apatite minerals.

The conservative behavior of phosphate is best appreciated in relation to Br^-, one of the most conservative ions in carbonate-rich lake brines because it forms highly soluble salts and does not significantly coprecipitate with other halides. In general, phosphate varies with Br^- along a 1:1 trend (the dashed line in the Br^- vs. phosphate plot in Fig. S1), which indicates that phosphate also behaves as a conservative ion. Other ions, such as Cl^- and Na^+, are also highly conservative and show a similar trend with phosphate.

The highest concentration ions in carbonate-rich lakes are invariably Na^+ and Cl^-. Sodium ion concentrations reach up to ~9 molal, at which point Na^+ precipitates as highly soluble NaCl and $NaHCO_3/Na_2CO_3$ phases. Similarly, Cl^- concentrations up to ~6 molal are possible before the Cl^- precipitates as halite (NaCl). In modern carbonate-rich lakes, phosphate concentrations above ~1 $mmol \cdot kg^{-1}$ commonly occur in brines saturated with respect to NaCl and $NaHCO_3/Na_2CO_3$ salts. K^+ ions have a similar chemistry to Na^+, but on average the K^+/Na^+ ratio in carbonate-rich lakes is ~0.05, and the highest concentrations are ~1 molal. Lower K^+ relative to Na^+ is caused by several factors. First, K^+ salts such as arcanite (K_2SO_4) and sylvite (KCl) are less soluble than their Na^+ analogs. Second, K^+ ions undergo irreversible ion exchange fixation and precipitates in secondary silicate minerals (1).

Other ions that have appreciable concentrations in carbonate-rich brines are boron species and SO_4^{2-}. Boron concentrations are especially high in Searles Lake (~0.4 molal) (2), although Owens lake in California also attains high boron concentrations during evaporation (3). Boron concentrations are limited by highly soluble borax salts ($Na_2B_4O_7 \cdot 10H_2O$) (4). On present-day Earth, boron derives from weathering of boron-enriched continental crust (5). Although less land was likely present at life's origin than today, trace boron could have accumulated in significant concentrations via evaporative concentration in closed-basin lakes even on small amounts of land, such as ocean islands. Finally, SO_4^{2-} reaches concentrations of ~1 molal before precipitating as Na^+ and K^+ salts such as mirabillite ($Na_2SO_4 \cdot 10H_2O$), arcanite, and thenardite (Na_2SO_4).

Ca^{2+} and Mg^{2+} ions generally have relatively low concentrations in carbonate-rich lakes, as expected based on high concentrations of carbonate ions. In some cases, Ca^{2+} and Mg^{2+} attain maximum concentrations of ~10 mM in carbonate-rich lakes; however, we question the accuracy of such high literature values. Almost all of the high Ca^{2+} values in Fig. S1 corresponding to high phosphate concentrations are from a single study (6). This study measured Ca^{2+} and Mg^{2+} using

Inductively Coupled Optical Emission Spectroscopy (ICP-OES); however, ICP-OES suffers from matrix effects when measuring trace components in concentrated solutions, which may raise the apparent ion concentration. Given that Ref. (6) gives little information on the analytical procedure, and that the Ca^{2+} and Mg^{2+} values are anomalously high, these measurements are of questionable accuracy. Other anomalously high Ca^{2+} values are from analyses done prior to ~1920, and so are also of questionable accuracy.

As an example of possible inaccuracies in literature Ca^{2+} analyses, Owens Lake, California, was analyzed prior to ~1920 and found to have ~1 mM Ca^{2+} (7). In comparison, a later study done by highly competent researchers measured 0.05-0.2 mM Ca^{2+} (3), which decrease with increasing carbonate alkalinity during evaporation as expected. We may also compare environmental Ca^{2+} concentrations with careful laboratory measurements of calcite solubility in Na_2CO_3 solutions (8), which indicate Ca^{2+} concentrations between 0.01-0.1 mM Ca^{2+} depending on the inorganic carbon concentration. Furthermore, we measured Ca^{2+} concentrations in several of the experimental brines in this manuscript (see SI Appendix B), and found that concentrations are ~0.1 mM.

Carbonate-rich lakes are rich in many other ions such as F^-, Li^+, silica, and trace metals (9-11). In particular, silica and trace metals accumulate because of the formation of more soluble ion complexes in the presence of high pH and/or high concentrations of background ions. Silica accumulates at relatively high concentrations in carbonate-rich lakes because $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ species form at high pH, instead of $H_4SiO_4^0$ species at low pH. Similarly, trace metals are relatively soluble in carbonate-rich lakes because they form complexes with concentrated Cl^-, OH^-, HCO_3^-, and CO_3^{2-} ions.

Finally, we note that phosphorus may be present in inorganic and organic forms. In most analyses presented in Fig. S1, phosphate is measured using colorimetric methods, which is sensitive only to dissolved inorganic phosphate; however, measurements of the bulk P content by atomic emission methods yields only the total dissolved P (inorganic + organic phosphorus). In these cases (e.g., the P analyses for Goodenough and Last Chance lakes), a fraction of the total measured dissolved P may be due to the dissolved organic phosphorus.

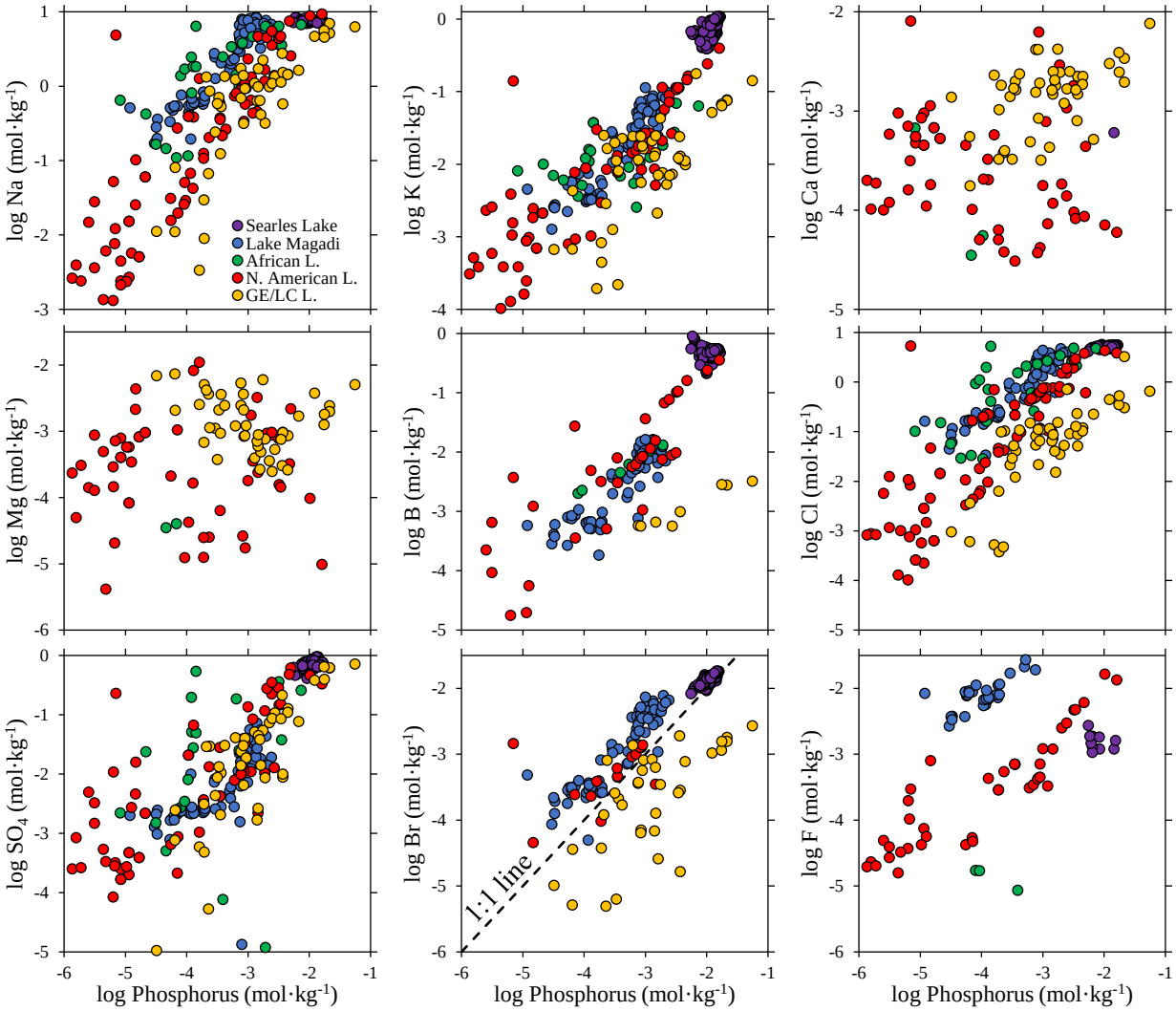

Fig. S1. Concentrations of P, Na^+, K^+, Ca^{2+}, Mg^{2+}, B, Cl^-, SO_4^{2-}, Br^-, and F^- in Searles Lake, Lake Magadi, Goodenough and Last Chance lakes (GE/LC L.), various other African lakes (African L.), and various other North American Lakes (N. American L.). We only plot lake compositions that have been analyzed for phosphate/phosphorus. The dashed line in the Br^- vs. phosphorus plot indicates the 1:1 trend expected for conservative solutes.

Appendix B: Results of experiments on gypsum addition to phosphate-rich brines

The results of our experiments on phosphate- and carbonate-rich brines in the lab are presented here. Table S1 describes the initial salt content of the solutions, the salt concentration after equilibration (calculated by accounting for ions precipitated in solid phases, as described in the *Methods* section), and the modeled pH, pCO_2, and $\%HCO_3$ in the equilibrated solution. Table S2 describes the composition of solid phases on a dry weight basis after equilibration, where the CO_3^{2-} content is calculated based on charge balance (as described in the *Methods* section). Finally, the XRD profiles of the solid phases listed in Table S2 are presented in Fig. S2 through Fig. S6.

To check our modeled pH values listed in Table S1, we also measured the pH of several solutions with a standard glass electrode, and found that the measured pH was typically within 0.2 of the modeled value. We note that pH measurements in salt solutions are complicated by several sources of error, such as theoretical uncertainties on the value of single ion activity coefficients in concentrated solutions and liquid junction potential errors (12). Another possible issue is that the modeled pH is sensitive to errors in the composition of the precipitated salts, which we subtract from the initial prepared solution composition to arrive at the final solution composition. First, measured ion concentrations have likely errors of approximately ±5 % based on the accuracy of ICP-OES analyses. Second, errors in the assumed ionic speciation of the solid phases can affect the modeled pH. For precipitated solids, we assumed that only CO_3^{2-} and PO_4^{3-} ions were present, based on solids identified via XRD, but HCO_3^- and HPO_4^{2-} ions may also have been present in the solids. Removing CO_3^{2-} and PO_4^{3-} ions from the initial solution results in a lower modeled pH than if HCO_3^- and HPO_4^{2-} ions are removed. This is because CO_3^{2-} and PO_4^{3-} ions have more alkalinity than equivalent concentrations of HCO_3^- and HPO_4^{2-} ions.

Another key assumption in our analysis is that all of the Ca^{2+} in the experimental solutions remained in solid phases. We tested this by measuring Ca^{2+} in a representative suite of four samples using ICP-OES (sample numbers 1, 8, 9, and 11 in Table S1). To achieve the highest possible accuracy, we corrected for matrix effects by spiking each sample with known amounts of Ca^{2+}, and ensuring that no precipitates formed by acidifying with HNO_3. Each sample was analyzed with no added Ca^{2+}, followed by three replicate samples with increasing amounts of Ca^{2+}. We then calculate the Ca^{2+} in the unspiked samples by linear regression of the spiked samples. The lowest concentration of Ca^{2+} that we spiked the samples with was 0.1 $mmol \cdot kg^{-1}$. Our results indicate that Ca^{2+} concentrations are 0.07, 0.11, 0.045, and 0.033 $mmol \cdot kg^{-1}$ for sample numbers 1, 8, 9, and 11 respectively in Table S1. For an initial added Ca^{2+} concentration of 100 $mmol \cdot kg^{-1}$, this means that ~99.9 % of the added Ca^{2+} remained in solid phases over the course of the experiment.

Table S1. The concentration of ions (molal) in the initial and final solutions equilibrated over 1 to 4 weeks. The initial total molality is the molality of all salts initially added to the experiment, including gypsum. The final aqueous molality is the solution molality after equilibration, which is calculated by assuming all Ca^{2+} is present in solid phases, and subtracting ions precipitated in solid phases (see Table S2) from the initial total molality. Finally, the modeled values for the equilibrated solution were determined by modeling gas-solution equilibrium with 100 ml of headspace (as in the experimental set-up) using the geochemical program PHREEQC and the aqueous database THEREDA.

		Initial Total Molality						Final Aqueous Molality					Modeled Aqueous Values		
#	Time	Na	Ca	SO_4	C	P	F	Na	SO_4	C	P	F	pH	$\log_{10}(pCO_2)$	$\%HCO_3$
	weeks						molal							bars	
	Series 1: Variable HCO_3:CO_3 ratio, with and without fluoride														
1	2	1.19	0.099	0.099	1.09	0.049		1.17	0.099	1.04	0.014		7.03	0.48	99.4
2	2	1.2	0.099	0.099	1.09	0.049		1.19	0.099	1.04	0.011		7.11	0.41	99.3
3	2	1.21	0.099	0.099	1.09	0.049		1.2	0.099	1.03	0.021		7.16	0.36	99.2
4	2	1.23	0.099	0.099	1.09	0.049		1.23	0.099	1.03	0.021		7.3	0.22	98.9
5	2	1.26	0.099	0.099	1.09	0.049		1.25	0.099	1.03	0.025		7.49	0.04	98.3
6	2	1.28	0.099	0.099	1.09	0.049		1.27	0.099	1.01	0.033		7.71	-0.19	97.2
7	2	1.65	0.099	0.099	1.29	0.049		1.64	0.099	1.19	0.049		8.67	-1.17	76.4
8	2	2.32	0.099	0.099	1.59	0.049		2.26	0.099	1.46	0.048		9.11	-1.72	48.6
9	2	3.43	0.099	0.099	2.08	0.049		3.23	0.099	1.88	0.048		9.39	-2.13	28.5
10	2	5.46	0.099	0.099	2.98	0.049		5.31	0.099	2.81	0.049		9.78	-2.73	12
11	2	5.06	0.099	0.099	2.48	0.049		4.91	0.099	2.31	0.048		11.05	-5.25	0.8
12	2	1.04	0.05	0.05	0.93	0.05	0.009	1.03	0.05	0.92	0.025	0.009	7.44	0.05	98.6
13	2	1.21	0.05	0.05	1.1	0.05	0.009	1.21	0.05	1.08	0.027	0.009	7.56	0	98.1
14	2	1.23	0.05	0.05	1.1	0.05	0.009	1.22	0.05	1.08	0.028	0.009	7.68	-0.12	97.5
15	2	1.25	0.05	0.05	1.1	0.05	0.009	1.24	0.05	1.07	0.034	0.009	7.9	-0.35	95.8
16	2	1.27	0.05	0.05	1.1	0.05	0.009	1.27	0.05	1.06	0.036	0.009	8.13	-0.59	93
17	2	1.29	0.05	0.05	1.1	0.05	0.009	1.29	0.05	1.06	0.037	0.009	8.3	-0.78	89.8
18	2	1.43	0.05	0.05	1.1	0.05	0.009	1.43	0.05	1.05	0.049	0.009	8.83	-1.4	70.7
19	2	2.01	0.05	0.05	1.36	0.05	0.009	2	0.05	1.3	0.049	0.009	9.21	-1.89	44.6
20	2	2.95	0.05	0.05	1.78	0.05	0.009	2.92	0.05	1.71	0.05	0.009	9.48	-2.29	25.9
21	2	4.68	0.05	0.05	2.54	0.05	0.009	4.64	0.05	2.47	0.049	0.009	9.83	-2.85	11.4
22	2	4.34	0.05	0.05	2.12	0.05	0.009	4.28	0.05	2.04	0.049	0.009	11.13	-5.45	0.7
	Series 2: Variable equilibration time, without fluoride														
23	1	2.33	0.099	0.099	1.59	0.049		2.2	0.099	1.43	0.048		9.09	-1.69	50.3
24	2	2.33	0.1	0.1	1.59	0.05		2.27	0.099	1.47	0.049		9.11	-1.72	48.6
25	3	2.32	0.099	0.099	1.59	0.049		2.32	0.099	1.49	0.049		9.13	-1.74	47.2
26	4	2.32	0.099	0.099	1.59	0.049		2.32	0.099	1.49	0.049		9.13	-1.74	47.2
	Series 3: Variable initial phosphate concentration, with and without fluoride														
27	2	2.07	0.099	0.099	1.34	0.099		2.06	0.099	1.24	0.098		9.13	-1.8	48.8
28	2	2.26	0.099	0.099	1.34	0.199		2.2	0.099	1.28	0.148		9.08	-1.73	50.7
29	2	2.46	0.099	0.099	1.34	0.298		2.39	0.099	1.29	0.243		9.05	-1.71	50.9
30	2	2.66	0.099	0.099	1.34	0.397		2.59	0.099	1.29	0.339		9.03	-1.7	51
31	2	2.86	0.099	0.099	1.34	0.497		2.8	0.099	1.3	0.436		9.01	-1.68	50.9
32	2	1.93	0.05	0.05	1.36	0.01	0.009	1.92	0.05	1.3	0.01	0.009	9.22	-1.9	44.5
33	2	1.95	0.05	0.05	1.36	0.02	0.009	1.94	0.05	1.3	0.02	0.009	9.22	-1.9	44.5
34	2	2.01	0.05	0.05	1.36	0.05	0.009	2	0.05	1.3	0.05	0.009	9.21	-1.89	44.6
35	2	2.1	0.05	0.05	1.36	0.099	0.009	2.1	0.05	1.31	0.096	0.009	9.2	-1.88	44.7
36	2	2.3	0.05	0.05	1.36	0.198	0.009	2.29	0.05	1.33	0.182	0.009	9.16	-1.85	45.1

Table S2. The concentration of ions (wt. %) in solid phases after equilibration of the solutions given in Table S1, and drying at 60°C in a vacuum oven overnight. Na, Ca, P, and S were measured using inductively coupled optical emission spectroscopy (ICP-OES), whereas the CO_3^{2-} content was calculated via charge balance (see Methods). Phases determined via XRD analysis (presented in Fig. S2 through Fig. S6) are given in the last column.

#	Na	Ca	PO_4	SO_4	CO_3	Total	XRD Phases
			wt. %				
	Series 1: Variable HCO_3:CO_3 ratio, with and without fluoride						
1	3.46	33.34	28.66	0.77	26.88	93.12	calcite, apatite
2	2.52	37.7	34.88	0.06	26.75	101.91	calcite, apatite
3	1.81	38.12	26.02	0.46	34.59	101	calcite, apatite
4	2.08	37.47	25.31	0.3	34.75	99.91	calcite, apatite
5	1.82	36.93	21.42	0.22	37.34	97.73	calcite, apatite
6	1.37	37.99	15.08	0.25	44.33	99.01	calcite, apatite
7	0.79	39.09	0.85	0.13	58.78	99.65	calcite
8	9.68	27.25	0.62	0.14	52.83	90.53	calcite, gaylussite
9	20.25	17.07	0.42	0.15	51.53	89.41	calcite, gaylussite
10	18.26	20.95	0.42	0.34	54.64	94.61	calcite, gaylussite
11	18.47	20.63	0.54	0.4	54.28	94.31	calcite, gaylussite
12	2.61	36.98	43.1	0	18.03	100.72	apatite
13	2.91	35.84	38.6	0.09	20.93	98.36	calcite, apatite
14	2.84	36.9	38.56	0.1	22.45	100.86	calcite, apatite
15	2.75	37.31	28.55	0.2	32.37	101.17	calcite, apatite
16	2.18	38.47	24.8	0.1	36.99	102.53	calcite, apatite
17	2.12	38.03	22.32	0	38.67	101.14	calcite, apatite
18	0.53	39.68	0.98	0	59.29	100.49	calcite
19	0.65	39.98	0.21	0	60.62	101.45	calcite
20	12.07	27.46	0.08	0	56.86	96.47	calcite, gaylussite
21	14.33	26.47	0.21	0.1	58.14	99.25	calcite, gaylussite
22	17.8	23.06	0.68	0.09	57.12	98.75	calcite, gaylussite
	Series 2: Variable equilibration time, without fluoride						
23	16.37	22.17	0.7	0.2	53.83	93.28	calcite, gaylussite
24	9.68	27.25	0.62	0.14	52.83	90.53	calcite, gaylussite
25	1.06	39.52	0.57	0.08	60.08	101.31	calcite
26	0.96	38.82	0.69	0.08	58.78	99.33	calcite
	Series 3: Variable initial phosphate concentration, with and without fluoride						
27	1.13	38.57	1.07	0.11	58.25	99.13	Ca-Na phosphate
28	10.13	27.13	33.02	0.32	22.42	93.02	Ca-Na phosphate
29	10.99	27.63	36.33	0.41	21.09	96.45	Ca-Na phosphate
30	11.02	27.11	37.84	0.58	18.82	95.37	Ca-Na phosphate
31	10.31	28.04	40.47	0.5	16.85	96.16	calcite
32	0.57	40.05	0.03	0	60.79	101.43	calcite, apatite
33	0.55	38.83	0.06	0	58.91	98.35	calcite, apatite
34	0.58	40.19	0.18	0	60.88	101.82	calcite
35	1.07	38.79	5.68	0	54.2	99.73	calcite
36	3.62	35.89	28.86	0	31.21	99.58	calcite

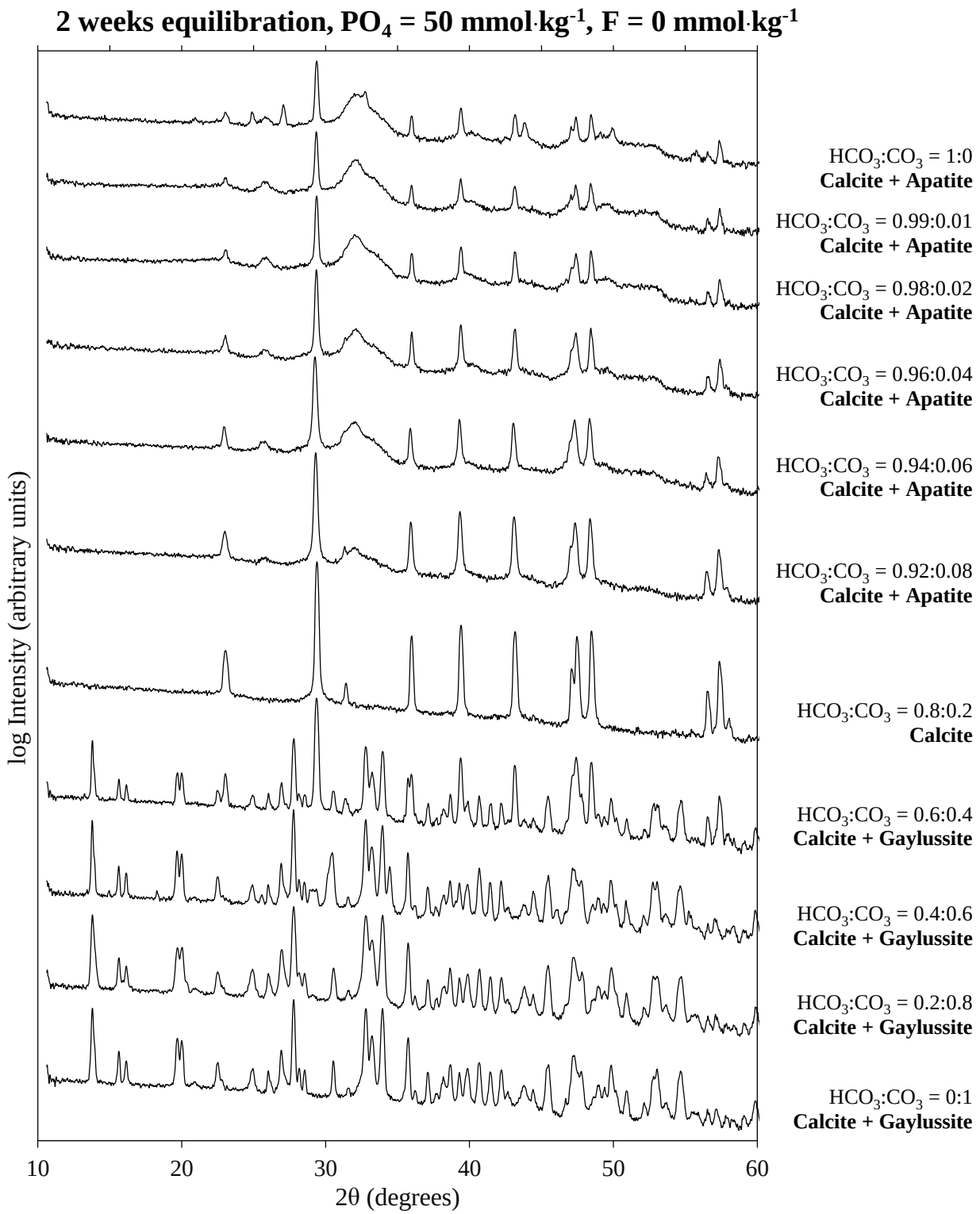

Fig. S2. XRD profiles of saturated carbonate brines containing 50 mmol·kg^{-1} phosphate (no added F^-) equilibrated for two weeks at various HCO_3:CO_3 ratios. This corresponds to sample numbers 1 to 11 in Table S1 and Table S2.

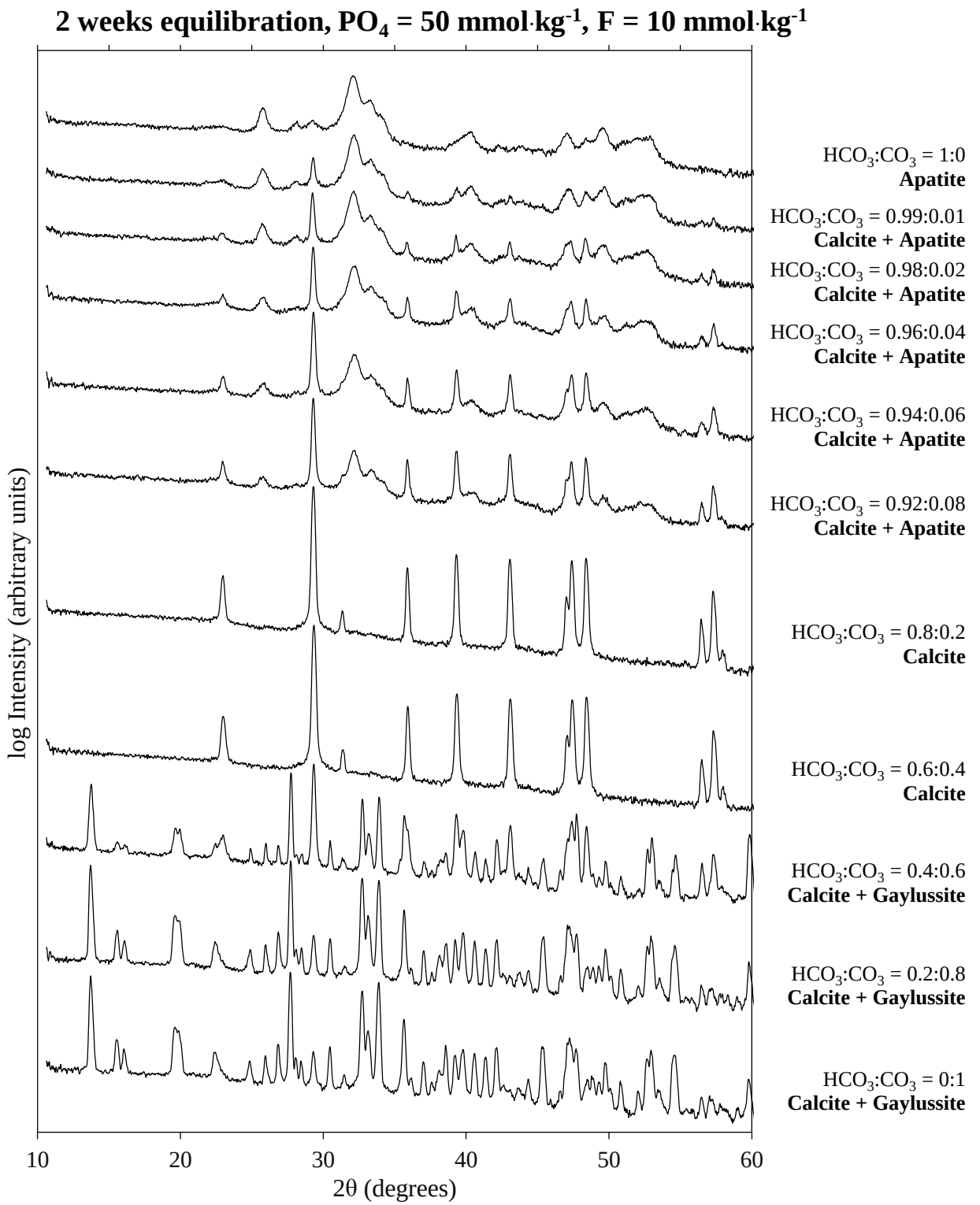

Fig. S3. XRD profiles of saturated carbonate brines containing 50 mmol·kg^{-1} phosphate and 10 mmol·kg^{-1} F^- equilibrated for two weeks at various molar HCO_3:CO_3 ratios. This corresponds to sample numbers 12 to 22 in Table S1 and Table S2.

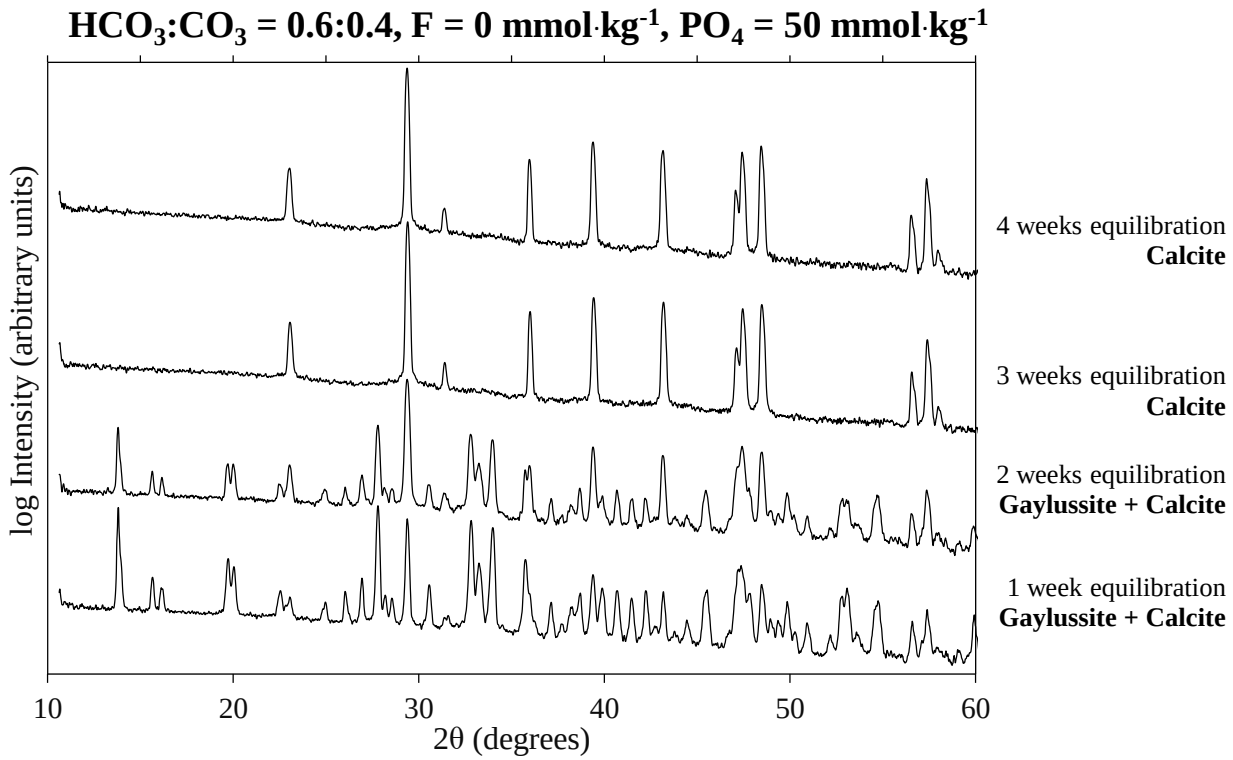

Fig. S4. XRD profiles of saturated carbonate brines with a molar HCO_3:CO_3 ratio of 0.6:0.4 (no added F^-) and an initial phosphate concentration of 50 mmol·kg^{-1} equilibrated over one to four weeks. This corresponds to sample numbers 23 to 26 in Table S1 and Table S2.

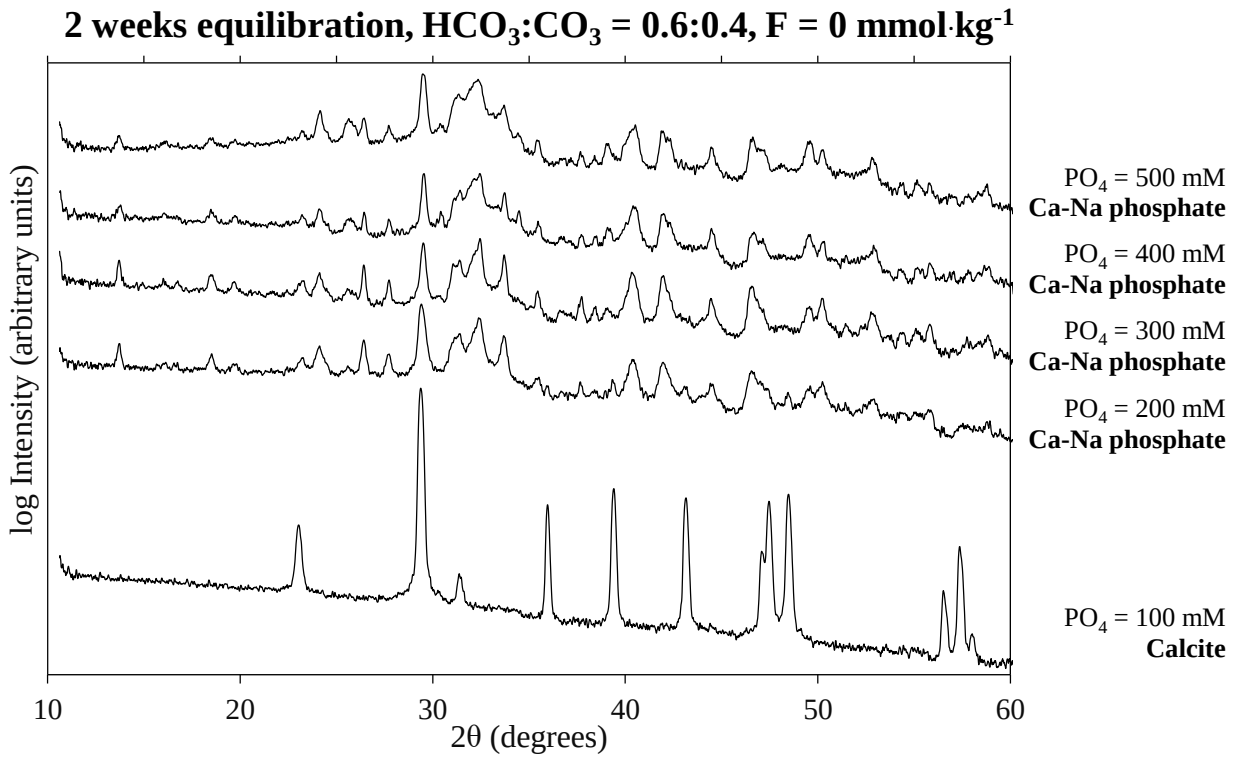

Fig. S5. XRD profiles of saturated carbonate brines with a molar HCO_3:CO_3 ratio of 0.6:0.4 (no added F^-) equilibrated for two weeks at various initial phosphate concentrations. This corresponds to sample numbers 27 to 31 in Table S1 and Table S2.

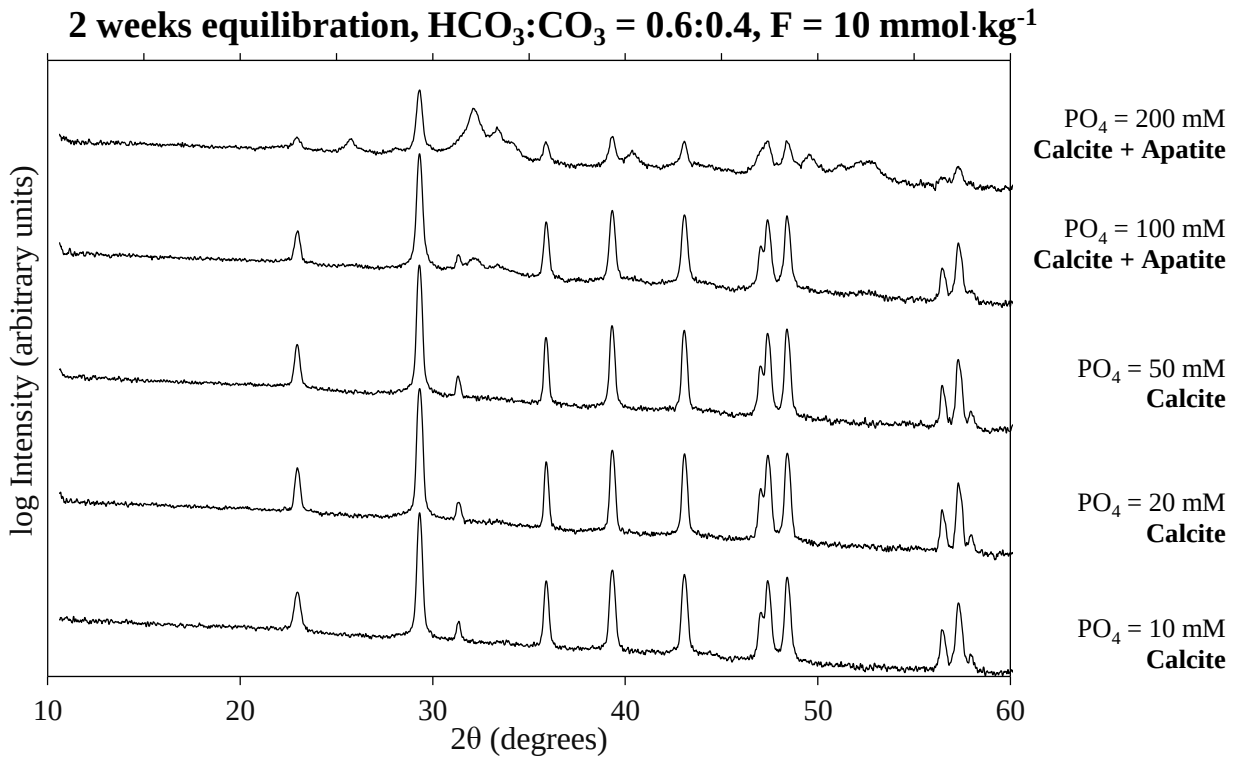

Fig. S6. XRD profiles of saturated carbonate brines with a molar HCO_3:CO_3 ratio of 0.6:0.4 and 10 mmol·kg^{-1} F^- equilibrated for two weeks at various initial phosphate concentrations. This corresponds to sample numbers 32 to 36 in Table S1 and Table S2.

Appendix C: Geochemical models

The Pitzer model

To model concentrated solutions in the Na-Cl-P-CO_2-H-OH system, we use the Pitzer model (13). The Pitzer equation for the excess Gibbs energy of solution (G^{EX}) in a mixed aqueous salt solution containing cations c and anions a is given by:

$$G^{EX} = -4A_\phi \ln\left(1+b\sqrt{I}\right)\frac{I}{b} + \sum_c\sum_a m_c m_a \left(2\beta_{ca} + ZC_{ca}\right) + \sum_c\sum_{c'} m_c m_{c'}\left(2\Phi_{cc'} + m_a\sum_a \psi_{cc'a}\right) + \sum_a\sum_{a'} m_a m_{a'}\left(2\Phi_{aa'} + m_c\sum_c \psi_{aa'c}\right) \quad (1)$$

In this equation, subscript *M* indicates a cation, subscript *X* indicates an anion, *c'* is a cation different from *c*, *a'* is an anion different from *a*, *b* is a constant (1.2 $kg^{-1/2}\cdot mol^{-1/2}$), *I* is the ionic strength given by $I = \frac{1}{2}\sum m_i z_i^{\,2}$, z_i is the ion charge, *Z* is given by $Z = \sum m_i |z_i|$, and A_ϕ is the Debye–Hückel limiting law slope. Differentiation of G^{EX} with respect to moles of water (n_1) and salt (n_i) at molality *m* ($mol\cdot kg^{-1}$) leads to expressions for the activity coefficients for water (a_w) and salt (γ) respectively:

$$\frac{\partial G^{EX}}{\partial n_1} = RT\ln a_w \quad \text{and} \quad \frac{\partial G^{EX}}{\partial n_i} = RT\ln m_i\gamma_i \quad (2)$$

Importantly, water activities are commonly reported as osmotic coefficients (ϕ), which are related by the equation:

$$\phi = -55.50844\frac{\ln a_w}{\sum m_i} \quad (3)$$

The parameters β, C, and Φ are given by the functions:

$$\beta_{ca} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} g(\alpha_1\sqrt{I}) + \beta_{ca}^{(2)} g(\alpha_2\sqrt{I}) \quad (4)$$

$$C_{ca} = \frac{C_{ca}^{\phi}}{2\sqrt{|z_c z_a|}} \quad (5)$$

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij} \quad (6)$$

where ${}^{E}\theta_{ij}$ is a higher-order electrostatic terms that account for interactions between ions of the same sign, but different charge (i.e. $z_i \neq z_j$), and $g(x)$ is given by:

$$g(x) = \frac{2\left[1-\left(1+x\right)e^{-x}\right]}{x^2} \quad (7)$$

Finally, equilibrium between an aqueous solution and a hydrated salt with x water molecules, ν_c cations, and ν_a anions is described by the precipitation/dissolution reaction:

(8) $$M_{\nu_c}X_{\nu_a}\cdot xH_2O(s) = \nu_c M^{z_c} + \nu_a X^{z_a} + xH_2O$$

where the thermodynamic equilibrium constant K for this reaction may be calculated from the ion activity product of the saturated solution:

(9) $$K = \left(m_c\gamma_c\right)^{\nu_c}\left(m_a\gamma_a\right)^{\nu_a} a_w^x$$

These equations indicate that the Pitzer equations describe properties in mixed electrolyte solutions using the temperature dependent Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ}, θ, and ψ, equilibrium constants K, and temperature-invariant parameters α_1 and α_2. For Pitzer parameters, PHREEQC uses the temperature dependent expression:

(10) $$P = a_0 + a_1\left(\frac{1}{T}-\frac{1}{T_r}\right) + a_2\ln\left(\frac{T}{T_r}\right) + a_3\left(T-T_r\right) + a_4\left(T^2-T_r^2\right) + a_5\left(\frac{1}{T^2}-\frac{1}{T_r^2}\right)$$

where a_i are empirical fitted parameters, T_r is a reference temperature at 298.15 K, and P is a Pitzer parameter. For equilibrium constants, PHREEQC uses the temperature dependent expression:

(11) $$\log K = a_1 + a_2T + \frac{a_3}{T} + a_4\log T + \frac{a_5}{T^2} + a_6T^2$$

Fits to experimental data on phosphate solubility

Experimental data on pure saturated sodium phosphate solutions are taken from Seidel (14), and fit to the Pitzer model described above by least-squares-minimization. The experimental data and the resulting model fits are given in Fig. S7.

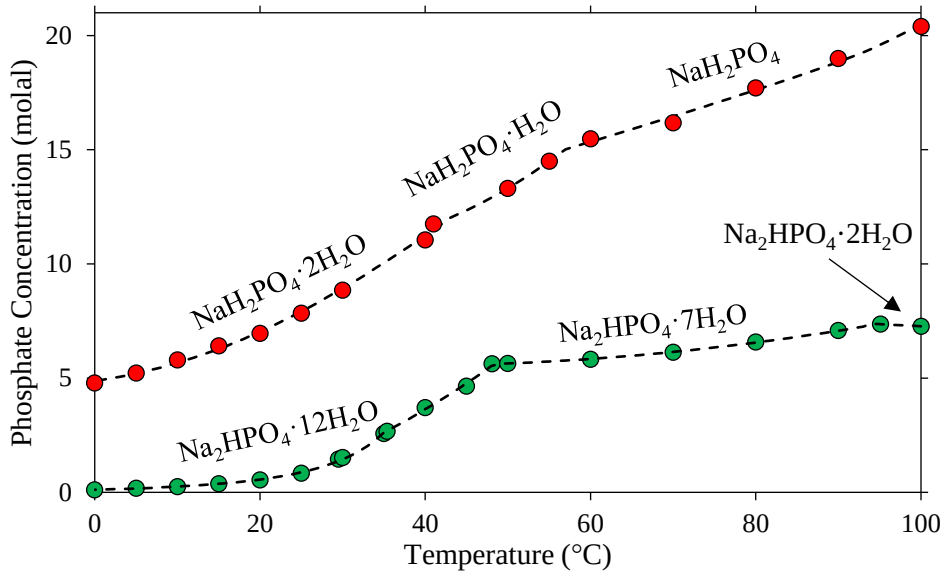

Fig. S7. Experimental solubility measurements (molal) for saturated sodium phosphate solutions at variable temperature for NaH_2PO_4 (red circles) and Na_2HPO_4 (green circles) salts. The modeled solubility of these salts is given as dashed lines.

PHREEQC database file

The following PHREEQC input code was used to model the solubility of phosphate salts in the Na-Cl-P-CO_2-H-OH system over a temperature range of 0 to 100°C. The interactive version of PHREEQC is available at https://www.usgs.gov/software/phreeqc-version-3/. If using the interactive version of PHREEQC, the definitions of all input parameters given below are well-described in the program. We have commented on the code primarily to specify the source reference for specific parameters.

```
# Parameters for chloride and carbonate salts and CO2 gas are taken from:
# Marion, G. M., et al. (2011).
# Modeling hot spring chemistries with applications to martian silica formation.
# Icarus 212(2): 629–642.

# Parameters for phosphate salts are taken from:
# Scharge, T., et al. (2013).
# Thermodynamic modelling of high salinary phosphate solutions. I. Binary systems.
# The Journal of Chemical Thermodynamics 64: 249-256.
# Scharge, T., et al. (2015).
# Thermodynamic modeling of high salinary phosphate solutions II. Ternary and higher systems.
# The Journal of Chemical Thermodynamics 80: 172-183.

PITZER
-MacInnes false
-use_etheta true
-redox false

SOLUTION_MASTER_SPECIES
H H+ -1. H 1.008
H(1) H+ -1. 0.0
E e- 0.0 0.0 0.0
O H2O 0.0 O 15.999
O(-2) H2O 0.0 0.0
Na Na+ 0.0 Na 22.99
Cl Cl- 0.0 Cl 35.45
```

```
C CO3-2 2.0 HCO3 12.015
C(4) CO3-2 2.0 HCO3 12.015
P PO4-3 0 94.973 30.973762
P(5) PO4-3 0 94.973

SOLUTION_SPECIES
H+ = H+
 log_k 0

e- = e-
 log_k 0

H2O = H2O
 log_k 0

Na+ = Na+
 log_k 0

Cl- = Cl-
 log_k 0

CO3-2 = CO3-2
 log_k 0

PO4-3 = PO4-3
 log_k 0

H2O = OH- + H+
-analytic -2.2219506201E+02 -5.5058066492E-01 -1.4737247297E+04 1.5156364455E+02 7.7093244810E+05 4.2832724439E-04

CO3-2 + H+ = HCO3-
-analytic 7.8843549125E+01 2.8114156336E-02 -3.5739677566E+03 -2.8384191832E+01 4.7335781578E+05 0

CO3-2 + 2 H+ = CO2 + H2O
-analytic 3.3245684222E+02 7.3424990888E-02 -1.9829264031E+04 -1.1794430937E+02 1.8387797092E+06 0

2H+ + PO4-3 = H2PO4-
 log_k 19.562
 -delta_h -4.520 kcal

3H+ + PO4-3 = H3PO4
 log_k 21.702
 -delta_h -10.1 kJ

H+ + PO4-3 = HPO4-2
 log_k 12.35
 -delta_h -3.530 kcal

PHASES
Halite # From Marion et al. 2011
 NaCl = Cl- + Na+
-analytic -1.2527916896E+02 -1.5940706427E-01 -7.1582997565E+00 6.6592262608E+01 -7.6881371104E-02 1.0843908037E-04

Na2CO3:7H2O # From Marion et al. 2011
 Na2CO3:7H2O = 2Na+ + CO3-2 + 7H2O
-analytic -1.0242414096E+01 3.2849157355E-02 0 0 0 0

Na2CO3:H2O # From Marion et al. 2011
 Na2CO3:H2O = 2Na+ + CO3-2 + H2O
-analytic -2.8774550065E+01 1.8458757574E-01 0 0 0 -2.9016373919E-04

Nahcolite # From Marion et al. 2011
 NaHCO3 = HCO3- + Na+
-analytic 2.7096628475E+02 4.6935820304E-01 1.5642665039E+01 -1.5204447068E+02 1.6854829142E-01 -3.9508831422E-04
```

Natron # From Marion et al. 2011
 Na2CO3:10H2O = CO3-2 + 2 Na+ + 10H2O
-analytic -5.9688261032E+00 -7.4737824292E-03 0 0 0 8.3268627375E-05

Trona # From Marion et al. 2011
 Na3H(CO3)2:2H2O = 3Na+ + HCO3- + CO3-2 + 2H2O
-analytic -1.01750000E+00 1.28307435E-02 -9.59229969E+01 -1.39706624E+00 2.82831158E+03 -8.84486220E-07

Na2(HPO4):12H2O # From this study.
 Na2(HPO4):12H2O = H+ + 12H2O + 2Na+ + PO4-3
 -analytical_expression -81.310371231 0.39641732552 0 0 0 -0.00057403221891

Na2(HPO4):7H2O # From this study.
 Na2(HPO4):7H2O = 7H2O + HPO4-2 + 2Na+
 -analytical_expression -53.300652324 0.31115586643 0 0 0 -0.00046145146621

Na2(HPO4):2H2O # From this study.
 Na2(HPO4):2H2O = 2H2O + HPO4-2 + 2Na+
 -analytical_expression 9.7729128374 -0.059178506134 0 0 0 8.4416737735e-05

Na2(HPO4) # From this study.
 Na2(HPO4) = HPO4-2 + 2Na+
 -analytical_expression 13.896733053 -0.059661090262 0 0 0 5.7293521435e-05

Na(H2PO4):2H2O # From this study.
 Na(H2PO4):2H2O = 2H+ + 2H2O + Na+ + PO4-3
 -analytical_expression -10.856644409 -0.082448426323 0 0 0 0.00018313420267

Na(H2PO4):H2O # From this study.
 Na(H2PO4):H2O = 2H+ + H2O + Na+ + PO4-3
 -analytical_expression 46.342978362 -0.43751747619 0 0 0 0.00073603174603

Na(H2PO4) # From this study.
 Na(H2PO4) = 2H+ + Na+ + PO4-3
 -analytical_expression -17.735301819 -0.0278227 0 0 0 8.6142857143e-05

CO2(g) # From Marion et al. 2011
 CO2 = CO2
-analytic 7.6172730397E+01 1.4954581339E-02 -5.1694861624E+03 -2.8759485533E+01 5.6914636107E+05 0.0000000000E+00

PITZER
-B0
The following are from Marion et al. 2011
H+ Cl- 1.9794612033E-01 4.3930392007E-02 2.6162364573E-04 -5.3121505493E-04 3.4074178888E-10 -1.3794988905E+00
Na+ Cl- 7.6273259396E-02 -1.0677687696E+03 -5.2850452529E+00 9.0310652648E-03 -2.5394712901E-06 1.4568462343E+04
Na+ CO3-2 3.6204808669E-02 1.1083789213E+03 1.1198570286E+01 -2.3301689083E-02 1.4225931266E-11 -1.0139889781E-01
Na+ HCO3- 2.8002054979E-02 6.8287100127E+02 6.8994999437E+00 -1.4459103667E-02 -1.0139500105E-10 4.8617733194E-01
Na+ OH- -7.9555220526E-02 2.0309032437E+04 1.6146658627E+02 -5.2616228562E-01 2.9653500975E-04 -5.1829489159E+05
The following are from Scharge et al. 2013, 2015
Na+ H2PO4- -0.0436
Na+ HPO4-2 -0.0172
Na+ PO4-3 0.15641

-B1
The following are from Marion et al. 2011
H+ Cl- 1.7663995597E-01 -4.4613022946E+04 -3.1259930375E+02 9.5812792829E-01 -5.3080804721E-04 1.2316610809E+06
Na+ Cl- 2.8041722849E-01 -4.7934459033E+03 -6.9757728955E+01 2.2182662176E-01 -1.0800038619E-04 -3.1269129963E+05
Na+ CO3-2 1.5120691287E+00 4.4124805360E+03 4.4581885679E+01 -9.9890728880E-02 -2.3470887122E-10 1.0021144087E+00
Na+ HCO3- 4.4005226296E-02 1.1292842314E+03 1.1410242105E+01 -2.4464729852E-02 -7.4828259687E-10 3.3354784151E+00
Na+ OH- 2.5311163491E-01 1.4885507672E+04 1.1834672330E+02 -3.9540544436E-01 2.3380756117E-04 -3.7988491809E+05
The following are from Scharge et al. 2013, 2015
Na+ H2PO4- -0.03389
Na+ HPO4-2 1.2116
Na+ PO4-3 3.9397

-C0
The following are from Marion et al. 2011
H+ Cl- -2.8913465588E-03 1.0693004789E-02 5.5410207932E-05 1.7224827506E-05 -5.9323763662E-08 -3.7953644554E-01
Na+ Cl- 1.2711016441E-03 7.7695148783E+01 2.3007504621E-01 -8.0897946811E-05 -1.1941587694E-07 -2.0177121991E+03
Na+ CO3-2 0.0052
Na+ OH- 4.1159992172E-03 7.3302950838E+02 5.8279924019E+00 -2.0502290395E-02 1.2873934762E-05 -1.8707050080E+04
The following are from Scharge et al. 2013, 2015
Na+ H2PO4- 0.00605
Na+ HPO4-2 0.00585
Na+ PO4-3 -0.03498

-LAMDA
The following are from Marion et al. 2011
Cl- CO2 2.0480415080E-02 -3.3159597997E+04 -3.1582776282E+02 9.9643227553E-01 -5.2121983640E-04 -6.0314596673E-01
Na+ CO2 8.1474353447E-02 1.0939930101E+05 1.0470213325E+03 -3.3265653899E+00 1.7531997031E-03 1.2758007796E+00

-PSI
The following are from Marion et al. 2011
Cl- CO3-2 Na+ 8.6555626983E-03 -1.1578726767E+01 -1.1401251201E-01 4.4733586264E-04 -4.6816398956E-07 3.7067215792E+02
Cl- HCO3- Na+ -1.2777037089E-02 -1.1975486345E+01 -1.4023338938E-01 5.1084176969E-04 -5.9489945059E-07 4.5438567976E+02
Cl- OH- Na+ -0.006
HCO3- CO3-2 Na+ 0.002
Na+ H+ Cl- -0.0037
OH- CO3-2 Na+ -0.017
The following are from Scharge et al. 2013, 2015
Cl- H2PO4- Na+ -0.01208
Cl- HPO4-2 Na+ -0.00883
Cl- PO4-3 Na+ -0.00243
HPO4-2 H2PO4- Na+ 0.03781
PO4-3 HPO4-2 Na+ 0.00207
CO3-2 PO4-3 Na+ -0.01449774

-THETA
The following are from Marion et al. 2011
Cl- CO3-2 -0.02
Cl- HCO3- 0.03
Cl- OH- -0.05
HCO3- CO3-2 -0.04
Na+ H+ 0.036
OH- CO3-2 0.1
The following are from Scharge et al. 2013, 2015
Cl- H2PO4- 0.10037
Cl- HPO4-2 0.07083
Cl- PO4-3 0.24341
H2PO4- HPO4-2 -0.32361
PO4-3 HPO4-2 0.25528
CO3-2 PO4-3 0.19766089

-ZETA
The following are from Marion et al. 2011
H+ Cl- CO2 -4.7051879034E-03 1.6334349475E+04 1.5238364378E+02 -4.7047340910E-01 2.4052572265E-04 1.2740734776
Na+ Cl- CO2 -5.7153028547E-04 6.87905500E+03 7.3745255829E+01 -2.58005360E-01 1.4782317370E-04 -7.78048610E-01

-APHI
The following are from Marion et al. 2011
3.9147193099E-01 3.6897938637E+02 3.5956550857E+00 -1.2908353094E-02 9.5199168775E-06 4.7098725794E+01

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