

Oxidative Phosphorus Chemistry Perturbed by Minerals

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Table S1. List of Plausibly Prebiotic Minerals.

Name	Group	IMA Formula	Occurrence*	Reference
Diopside	Silicate	CaMgSi ₂ O ₆	CM,MA,MT,RM,UM	[1]
Kaolinite	Silicate	Al ₂ Si ₂ O ₅ (OH) ₄	HY	
Orthoclase	Silicate	KAlSi ₃ O ₈	GR,MA,SD,UM,ZR	
Antigorite	Silicate	Mg ₃ Si ₂ O ₅ (OH) ₄	CM,HY,SP,UM	
Forsterite	Silicate	Mg ₂ SiO ₄	CM,MA,MT,UM,UR	
Quartz	Oxide	SiO ₂	GR,HY,MT,SD,ZR	
Hematite	Oxide	Fe ₂ O ₃	CM,GR,HY,RM,VP	
Magnetite	Oxide	Fe ₃ O ₄	CM, GR, MA, MT, RM, SD, UM	
Schreibersite	Phosphide	(Fe,Ni) ₃ P	MT	
Gypsum	Sulfate	CaSO ₄ ·2H ₂ O	EV, LT, MT, PR, VP	
Siderite	Carbonate	FeCO ₃	AK, AU, GR, HY, UM	[2]
Calcite	Carbonate	CaCO ₃	AK,HY,MA,MT,PR	
Hydroxyapatite	Phosphate	Ca ₅ (PO ₄) ₃ OH	HY,SP	[3]
Newberyite	Phosphate	MgHPO ₄ ·3H ₂ O	HY	
Struvite	Phosphate	MgNH ₄ PO ₄ ·6H ₂ O	HY	
Ulexite	Borate	NaCaB ₅ O ₆ (OH) ₆ ·5H ₂ O	N/A	

* Modes of Occurrence: AK: alkali igneous; AU: authigenic; CM: contact metamorphism; EV: evaporite; GR: granitoid igneous; HY: hydrothermal alteration; LT: low-temperature metamorphism; MA: mafic igneous; MT: meteorite; PR: aqueous precipitate; RM: regional metamorphism; SD: clastic sedimentary environment; SP: serpentinization; UM: ultramafic igneous; UR: “ur-minerals” from pre-solar grains; VP: vapor phase deposition at volcanic fumaroles and other pneumolytic processes; ZR: inclusions in Hadean zircons.[1].

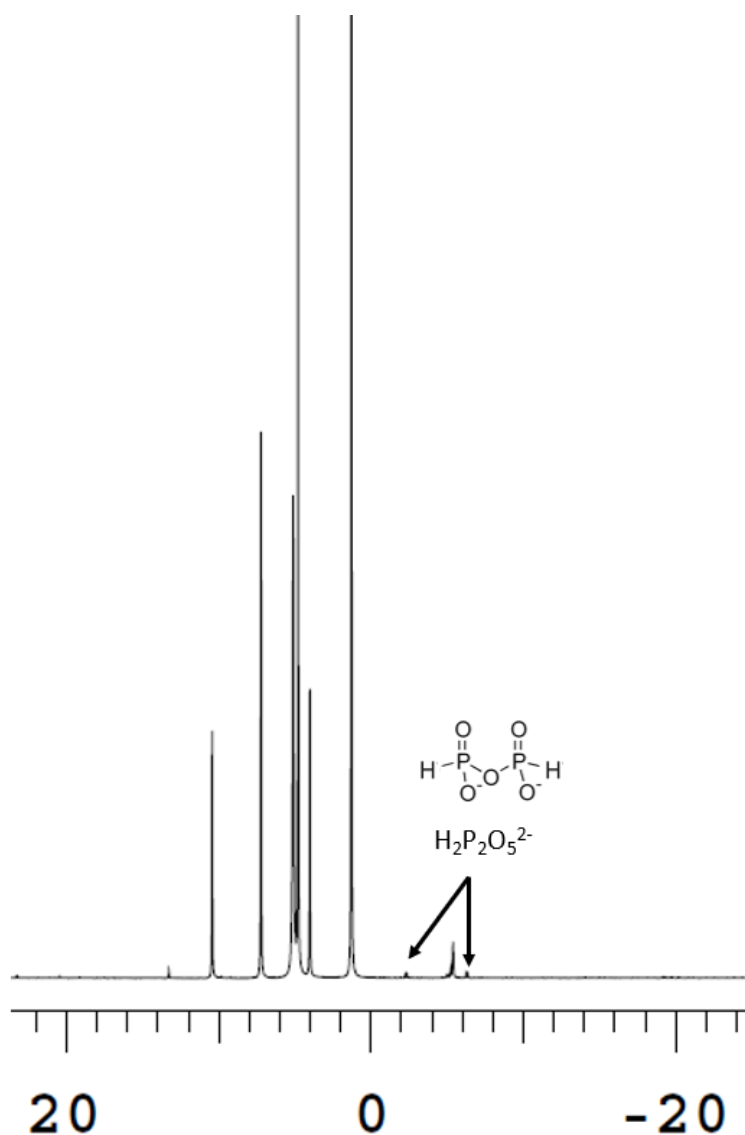


Figure S1. Fenton reaction with serpentinite and hypophosphite added. Peaks for pyrophosphite detected at -2.2 and -6.2 ppm.

Table S2. Hypophosphite Added Fenton reactions solutional product distribution table. All measurements are from peak integrations in the P31-NMR spectra.

No Minerals			Serpentinite			Schreibersite		
		Int. %			Int. %			Int. %
1	$\text{H}_2\text{PO}_2^{1-}$	23.1	1	$\text{H}_2\text{PO}_2^{1-}$	23.6	1	$\text{H}_2\text{PO}_2^{1-}$	0.5
2	HPO_3^{2-}	47.1	2	HPO_3^{2-}	50.7	2	HPO_3^{2-}	20
3	PO_4^{3-}	28.5	3	PO_4^{3-}	23.1	3	PO_4^{3-}	57.6
4	$\text{P}_2\text{O}_7^{4-}$	1.1	4	$\text{P}_2\text{O}_7^{4-}$	1.1	4	$\text{P}_2\text{O}_7^{4-}$	21.2
5	$\text{P}_2\text{O}_6^{4-}$	0.2	5	$\text{P}_2\text{O}_6^{4-}$	0.03	5	$\text{P}_3\text{O}_{10}^{5-}$	0.5
			6	$\text{H}_2\text{P}_2\text{O}_5^{2-}$	0.34	6	$\text{P}_2\text{O}_6^{4-}$	0.2
Hydroxyapatite			Kaolinite			Sand		
		Int. %			Int. %			Int. %
1	$\text{H}_2\text{PO}_2^{1-}$	11.5	1	$\text{H}_2\text{PO}_2^{1-}$	20.6	1	$\text{H}_2\text{PO}_2^{1-}$	22.6
2	HPO_3^{2-}	41	2	HPO_3^{2-}	48.1	2	HPO_3^{2-}	49.4
3	PO_4^{3-}	43.7	3	PO_4^{3-}	29.8	3	PO_4^{3-}	26.4
4	$\text{P}_2\text{O}_7^{4-}$	3.7	4	$\text{P}_2\text{O}_7^{4-}$	1.2	4	$\text{P}_2\text{O}_7^{4-}$	1.3
5	$\text{P}_2\text{O}_6^{4-}$	0.03	5	$\text{P}_2\text{O}_6^{4-}$	0.2	5	$\text{P}_2\text{O}_6^{4-}$	0.3

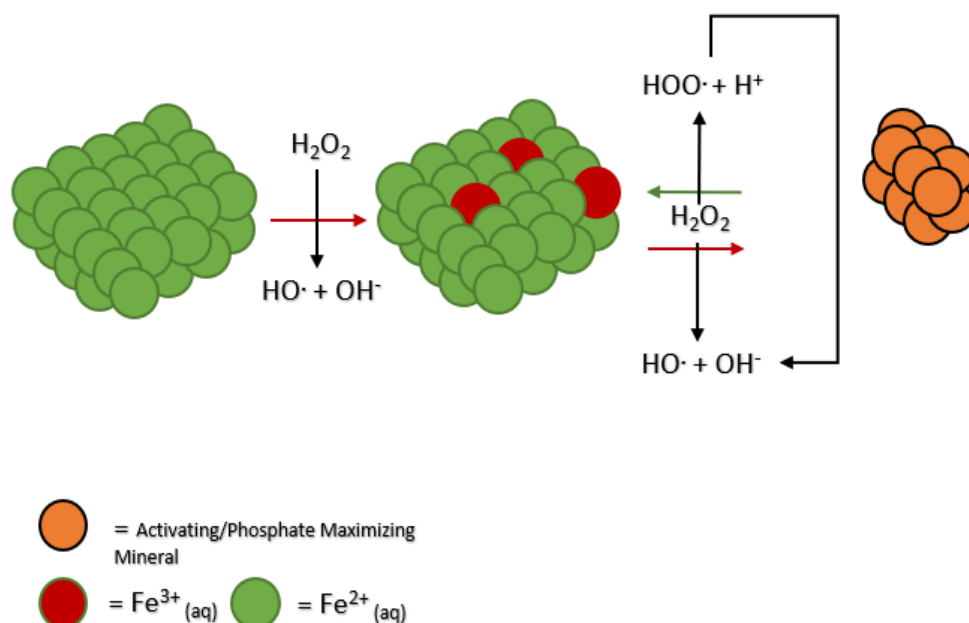


Figure S2. Additional Possible Fenton Reaction Diagram. Fenton reaction diagram showing a possible mechanism for increased oxidation by phosphate increasing minerals.

Table S3. ICPOES Data. The numbers refer to the counts for the solution phase P (before EDTA/NaOH extraction), mineral phase extracts (after EDTA/NaOH extraction), and extract/solution (count 1 divided by count 2). This is meant to show a before and after treatment so we can get an idea of the amount of P in solution and the amount of P in the mineral.

ICP OES Data					
	Solution Phase	Mineral Phase Extracts	Total P molarity	Fraction of P recovered (%)	Extract/Solution
Blank	9.17386E-06	2.14883E-05	3.06622E-05		
Calcite	0.051133892	0.011530277	0.062664169	62.66416894	18.40011188
Diopside	0.1001181	0.002866117	0.102984217	102.9842169	2.783064222
Gypsum	0.064682466	0.003267984	0.06795045	67.95045023	4.809362954
Hydroxyapatite	1.89739E-05	0.018070992	0.018089965	18.08996547	99.89511367
Hematite	0.069249782	0.00206493	0.071314712	71.31471223	2.895517907
Kaolinite	0.071491559	0.005637645	0.077129203	77.1292034	7.309351552
Magnetite	0.087120459	0.003514417	0.090634876	90.63487577	3.877555076
Newberyite	0.109277524	0.003267984	0.112545507	112.5455073	2.903699898
Olivine	0.073745617	0.001611778	0.075357395	75.35739521	2.138845607
Orthoclase	0.063897007	0.006769353	0.07066636	70.66636025	9.579314553
Sand	0.087929742	0.001871158	0.089800899	89.80089904	2.083673489
Schriebersite	0.1111905	0.006178802	0.117369302	117.3693023	5.264410941
Siderite	0.052652662	0.003111932	0.055764595	55.76459463	5.58048069
Serpentinite	0.082533096	0.00274475	0.085277847	85.27784664	3.218596937
Struvite	0.116365584	0.006552379	0.122917963	122.917963	5.330692685
Ulexite	0.064555406	0.009305467	0.073860873	73.86087333	12.59864261

Table S4. Mineral Extraction NMR Data. All measurements are from peak integrations in the P31-NMR spectra. The before group represents the solution phase before we extracted the sample with EDTA/NaOH. The after group represents the left-over P in the mineral phase liberated after EDTA/NaOH extraction.

NMR Data				
	Phosphite	Phosphate	Pyrophosphate	Triphosphate
Before				
Blank	21.6	52.6	23.2	2.6
Calcite	4.5	75	19.7	

Diopside	5.2	64	27.3	2.6	
Gypsum	21.7	63.7	14	0.6	
Hydroxyapatite	3.8	77	18.5	0.6	
Hematite	19.7	49.3	28	3	
Kaolinite	15	53.5	28.3	3.2	
Magnetite	31.6	40.9	25	2.5	
Newberyite	3.1	78.7	18.2		
Olivine	18.1	54.9	24.7	2.3	
Orthoclase	39.7	47.8	11.5	1	
Sand	14.2	54.7	28.4	2.7	
Schriebersite	11.5	52	33.3	3.1	
Siderite	17.6	48.7	30.7	3	
Serpentine	73.5	18.1	8.2	0.2	
Struvite	7.6	47.4	44.1	0.9	
Ulexite	1.5	73.5	25		
After	Phosphite	Pi	PPi	PPPi	Hypophosphate
Blank	17.1	58.8	24.1		
Calcite	2.6	64.1	33.3		
Diopside		55.5	44.5		
Gypsum	9.1	65	25.9		
Hydroxyapatite		85.5	14.5		
Hematite	37.5	37.8	24.6		
Kaolinite	16.2	54.1	29.7		
Magnetite	35.2	38.8	23.5		
Newberyite	7	70	23		
Olivine	32.8	39.5	27.7		
Orthoclase	14.8	52.9	32.3		
Sand	14.9	51.5	33.5		
Schriebersite	27.2	42.5	15.7	6	8.5
Siderite	23.7	43.1	33.2		
Serpentine	78	11.4	10.6		
Struvite	8.8	37	51.8	2.2	
Ulexite		57.5	42.5		

References

1. Hazen, R.M., *Paleomineralogy of the Hadean Eon: A preliminary species list*. American Journal of Science, **2013**. 313(9): P. 807-843.
2. Feng, T.; et al., *Evolution of Ephemeral Phosphate Minerals on Planetary Environments*. ACS Earth and Space Chemistry, **2021**. 5(7): P. 1647-1656.
3. Gull, M. and M.A. Pasek, *Catalytic Prebiotic Formation of Glycerol Phosphate Esters and an Estimation of Their Steady State Abundance under Plausible Early Earth Conditions*. Catalysts, **2021**. 11(11).