Effects of Organic Compounds on Dissolution of the Phosphate Minerals Chlorapatite, Whitlockite, Merrillite, and Fluorapatite: Implications for Interpreting Past Signatures of Organic Compounds in Rocks, Soils and Sediments

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Abstract

Phosphate is an essential nutrient for life on Earth, present in adenosine triphosphate (ATP), deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and phospholipid membranes. Phosphorus does not have a significant volatile phase, and its release from minerals is therefore critical to its bioavailability. Organic ligands can enhance phosphate release from minerals relative to release in inorganic solutions, and phosphorus depletion in paleosols has consequently been used as a signature of the presence of ligands secreted by terrestrial organisms on early Earth. We performed batch dissolution experiments of the Mars-relevant phosphate minerals merrillite, whitlockite, chlorapatite, and fluorapatite in solutions containing organic compounds relevant to Mars. We also analyzed these phosphate minerals using the ChemCam laboratory instrument at Los Alamos, providing spectra of end-member phosphate phases that are likely present on the surface of Mars. Phosphate release rates from chlorapatite, whitlockite, and merrillite were enhanced by mellitic, oxalic, succinic, and acetic acids relative to inorganic controls by as much as >35×. The effects of the organic compounds could be explained by the denticity of the ligand, the strength of the complex formed with calcium, and the solution saturation state. Merrillite, whitlockite, and chlorapatite dissolution rates were more strongly enhanced by acetic and succinic acids relative to inorganic controls (as much as >10×) than were fluorapatite dissolution rates (≲2×). These results suggest that depletion of phosphate in soils, rocks or sediments on Mars could be a sensitive indicator of the presence of organic compounds. Key Words: Mars—Phosphate—Merrillite—ChemCam—Organic compounds—Organomarker. Astrobiology 18, xxx–xxx.

1. Introduction

PHOSPHORUS, EITHER AS phosphate (Powner *et al.*, 2009) or as a more reduced form (Pasek and Block, 2009; Pasek and Kee, 2011), is considered essential for life to form. As phosphorus does not have a significant volatile phase, its release from minerals is critical to its bioavailability. On Earth, living organisms use phosphate to stabilize ribonucleic acid (RNA), deoxyribonucleic acid (DNA), and phospholipid membranes. Phosphate likely also played important roles in prebiotic chemistry including as a pH buffer and catalyst (Powner *et al.*, 2009). Phosphorus mobility from paleosols

under low-rainfall conditions has also been considered a proxy for organic compounds secreted by terrestrial organisms on early Earth (Neaman *et al.*, 2005).

Phosphate release from minerals is controlled by a variety of factors including mineralogy. Phosphate release by dissolution from Mars-relevant minerals such as merrillite and chlorapatite has been previously shown to differ significantly from phosphate release from fluorapatite, the dominant igneous phosphate phase on Earth (Adcock *et al.*, 2013). This previous work examined dissolution of Mars-relevant phosphate-bearing minerals over a range of pH values in inorganic solutions (Adcock *et al.*, 2013).

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Annually, 240 metric tons of organic material are deposited on Mars from carbonaceous chondrites and interplanetary dust particles (IDPs) (Flynn, 1996). The organic matter found in carbonaceous chondrites, and therefore likely to be deposited on Mars, encompasses a broad range of organic compounds including carboxylic acids, dicarboxylic acids, and sulfonic acids (Pizzarello *et al.*, 2006). Carboxylic acids are the most concentrated water soluble organic compounds in Murchison and other carbonaceous chondrites, with acetic acid as the most abundant carboxylic acid (Huang *et al.*, 2005). The highest concentration dicarboxylic acid in the Tagish Lake (CI2) meteorite is succinic acid (Pizzarello and Huang, 2002), and the highest concentration sulfonic acid in the Murchison meteorite is methylsulfonic acid (Cooper *et al.*, 1992).

In addition to the water soluble organic compounds, refractory organic matter (up to 3% of meteoritic material) (Hayes and Biemann, 1968) is also deposited on the martian surface (Derenne and Robert, 2010; Quirico *et al.*, 2014). Recent measurements by the Sample Analysis at Mars (SAM) instrument have detected the presence of organic predecessors to chlorobenzene, as well as a range of organic compounds (Freissinet *et al.*, 2015; Miller *et al.*, 2016; Eigenbrode *et al.*, 2018). Degradation products of refractory organic matter in martian soils would likely include benzenhexacarboxylic acid (*i.e.*, mellitic acid), as well as acetic and possibly oxalic acid, with concentrations of mellitic acid predicted based on theoretical work to reach 500 ppm (mg mellitic acid per kg soil) in martian soils after 3 billion years (Benner *et al.*, 2000), although measurements by SAM indicate organic concentrations in Yellowknife Bay of up to about 300 ppb (Freissinet *et al.*, 2015), and nanomolar concentrations in Mojave and Confidence Hills (Eigenbrode *et al.*, 2018). Acetic, succinic, and oxalic acids are also known to be produced by terrestrial microorganisms (Heyer and Krumbein, 1991; Prescott *et al.*, 1996; Madigan *et al.*, 2003).

Previous experimental work has shown enhanced dissolution of fluorapatite and hydroxyapatite in the presence of organic compounds (Tanaka *et al.*, 1989; Neaman *et al.*, 2005; Goyne *et al.*, 2006), and therefore dissolution of Mars-relevant phosphates would likely be impacted by organic compounds as well. To assess the effect of organic compounds on dissolution of phosphate minerals found in martian meteorites, we measured the dissolution rates of whitlockite, merrillite, chlorapatite, and fluorapatite in solutions containing five organic compounds likely present on Mars: acetic, succinic, oxalic, methylsulfonic, and mellitic acids. To the best of our knowledge, no prior studies have examined the effect of organic compounds on whitlockite, merrillite, or chlorapatite dissolution rates. We also performed laser-induced breakdown spectroscopy (LIBS) ChemCam analyses using the ChemCam laboratory instrument at Los Alamos to assess if these four phosphates can be distinguished on the martian surface by ChemCam and SuperCam.

Phosphate release rates from chlorapatite, whitlockite, and merrillite were enhanced by mellitic, oxalic, succinic, and acetic acids relative to inorganic controls by as much as >35×, with phosphate release rates from merrillite, whitlockite, and chlorapatite dissolution much more strongly enhanced by acetic and succinic acids (as much as >10×) than phosphate release rates from fluorapatite dissolution ($\lesssim 2\times$). These results suggest that depletion of phosphate in

martian rocks, soils and sediments may be a more sensitive indicator of past organic compounds than phosphate depletion in terrestrial rocks, soils and sediments.

2. Materials and Methods

2.1. Minerals

Three phosphate-bearing minerals were synthesized for use in dissolution experiments: whitlockite $[Ca_9Mg(PO_3OH)(PO_4)_6]$; merrillite $[Ca_{9.5}Mg(PO_4)_7]$ (Adcock *et al.*, 2013); and chlorapatite $[Ca_5(PO_4)_3Cl]$. Whitlockite was synthesized following the methods of Hughes *et al.* (2008) and Adcock *et al.* (2014). One gram of hydroxyapatite was mixed with 0.300 g magnesium nitrate in 90 mL 18.2 MΩ·cm^{-1} water. The mixture was acidified to a pH <2.8 with phosphoric acid and heated for 7 days at 240°C. Merrillite was also synthesized following Hughes *et al.* (2008) by heating whitlockite for 24–48 h at 1095°C; merrillite synthesized in this manner may contain traces of other minerals (Adcock *et al.*, 2014). Chlorapatite was synthesized by combining 3.12 g hydroxyapatite with 3.88 g calcium chloride and heating for 24 h at 1100°C (Prener, 1967, 1971; Tacker and Stormer, 1993; Dachs *et al.*, 2010). Fluorapatite $[Ca_5(PO_4)_3F]$ from Durango, Mexico was purchased from Minerals Unlimited (Ridgecrest, CA).

Each mineral was powdered, sieved, and cleaned before use in the dissolution experiments. Minerals were crushed in an agate mortar and pestle and then sieved to the size fraction 38–75 μm (400-200 mesh) for merrillite, chlorapatite, and whitlockite, and 75–150 μm (200-100 mesh) fraction for fluorapatite. The respective size fraction for each mineral was cleaned by sonicating in spectrographic grade ethanol at 3-min intervals, multiple times, until the supernatant was clear. BET surface areas of 0.0465 ± 0.0003 m^2/g for merrillite, 0.0516 ± 0.0002 m^2/g for whitlockite, 0.0563 ± 0.0004 m^2/g for chlorapatite, and 0.0321 ± 0.0002 m^2/g for fluorapatite (measured using Kr gas) were used from Adcock *et al.* (2013). Roughness factors (BET/Geometric Specific Surface Area ratio) can be highly variable (*e.g.* 2 to >900 for plagioclase) (White and Brantley, 2003). Roughness factors for these materials are <2, indicating that factors like mesoporosity and overall particle shape are not significantly increasing the BET measurements.

2.2. Batch dissolution experiments

For each dissolution experiment, 0.150 g of mineral (whitlockite, merrillite, chlorapatite, or fluorapatite) were measured into 250 mL polypropylene bottles and autoclave sterilized to prevent microbial contamination during experiments. One hundred and eighty milliliters of solution was added to the 250 mL polypropylene bottles. All solutions were made with 18.2 MΩ·cm^{-1} deionized water, and consisted of 0.01 *M* solutions of potassium nitrate, with or without the organic compound of interest adjusted to pH 5.5 using high purity nitric acid and potassium hydroxide and then filter-sterilized with a 0.2 μm polycarbonate filter. The pH of 5.5 was used to ensure that the organic compounds would be at least partially deprotonated, and thus able to complex Ca. Sodium acetate (>99% purity) and sodium succinate hexahydrate (98% purity) were purchased from Alfa Aesar. Sodium methyl sulfate (98% purity) and mellitic

acid (>98% purity) were purchased from TCI. Sodium oxalate (>99.5% purity) was purchased from Sigma-Aldrich. All organic compounds are referred to as organic acids in this work, although they are largely deprotonated as discussed section 3.5 below. Inorganic dissolution controls and mineral-free blanks were performed for each mineral-organic acid condition. Inorganic dissolution controls contained only potassium nitrate solution and mineral. Blanks were prepared with solutions containing no mineral. All experiments, blanks and controls were performed in duplicate.

All batch dissolution experiments were agitated at 100 rpm in a temperature-controlled shaking water bath at 25.0°C ± 0.1°C. Ten milliliters of solution was removed every hour for 6 h as well as once per day for the following 2 days. The pH was measured on a separate, unfiltered aliquot. The remaining sample was filtered using a 0.22 μm polypropylene filter and acidified to 1% v/v with high purity HNO_3 for subsequent analysis of phosphorus and calcium.

2.3. Analytical methods

Inorganic solutions and solutions containing acetic, succinic, methylsulfonic, and mellitic acids were analyzed for phosphorus concentrations using the colorimetric methyl blue/ascorbic acid method (Murphy and Riley, 1962). Absorbance was measured on a Thermo Scientific Genesys 10S ultraviolet–visible spectrophotometer at 882 nm wavelength. The absorbance of the colorimetric phosphate complex at 882 nm is linearly correlated to phosphate concentrations from 0.005 to 0.100 mM. Linear calibration curves based on six standards had R^2 values of 0.98 or better. Analytical uncertainty was estimated as 0.003 mM, based on the average of the standard errors of the regressions of the calibration curves.

Phosphate in samples containing oxalic acid could not be measured using the colorimetric ascorbic blue method. Therefore, samples containing oxalic acid were analyzed for phosphate using an iCAP Qc inductively coupled plasma mass spectrometer (ICP-MS) from ThermoFisher Scientific. Samples for ICP-MS analysis were diluted up to 40× with 18.2 MΩ·cm^{-1} water and acidified to 1% v/v with ultra-pure HNO_3. Calibration curves based on six standards had R^2 values of 0.99 or better, with lower and upper standards of 0.005 and 0.100 mM, respectively.

Calcium concentrations were measured using flame atomic absorption (AA) spectrometry on a Thermo Scientific, iCE 3000 Series AA spectrometer. To prevent phosphorus interference with calcium, 0.36 M lanthanum chloride was added to the samples at 10% v/v (APHA, 2005). The analytical uncertainty was estimated as 5% (APHA, 2005).

Calcium concentrations could not be determined for samples containing oxalic acid due to the formation of a precipitate. Goyne et al. (2006) also observed a decrease in calcium concentration during mineral dissolution in the presence of oxalic acid, attributing it to the likely formation of a calcium oxalate precipitate.

2.4. Solution chemistry modeling

2.4.1. Negatively charged ligands in solution. Using the mass action equation for ligand protonation and the log K values for each organic acid we calculated the total concentration of negatively charged ligands at the initial pH and final pH of each experiment.

2.4.2. PhreeqC modeling. Previous work has shown that the apparent solubility of fluorapatite is controlled by a leached layer with the composition of di-calcium phosphate anhydrous (DCPA) (Chairat et al., 2007). Making the assumption that such a leached layer is likely relevant to dissolution in our experiments, we determined the saturation index (SI) for the initial and sixth solution concentrations (the sixth sampling point is the final one used in the dissolution rate calculations) for each mineral experiment in inorganic solutions using the computer code PHREEQC (Parkhurst and Appelo, 1999) and the equilibrium constant for DCPA determined by Chairat et al. (2007). Where aqueous components were not measured (e.g., F and Cl for fluoroapatite and chlorapatite, respectively, and Mg for whitlockite and merrillite), release was assumed to be in a stoichiometric ratio with Ca, after Valsami-Jones et al. (1998).

2.4.3. Ca and P release. Moles of calcium and phosphorus released were calculated after Welch and Ullman (2000), by accounting for volume loss during sampling:

$$m_{(t)} = m_{(t-1)} + (c_{(t)} - c_{(t-1)}) \times V_{(t-1)} \qquad (1)$$

where $m_{(t)}$ is the moles released at time t, C is the concentration of calcium or phosphate measured at time t and $t-1$, and V is the volume of solution in L.

2.4.4. Mineral dissolution rates. Moles of calcium and phosphorus released (Eq. 1) as a function of time are fit with a linear regression, where the slope of the line is the rate of calcium or phosphorus release. The rate of dissolution of the mineral is then calculated from either the calcium or phosphate release rate using the expression below.

$$r_{diss} = \frac{\Delta m / \Delta t}{A \times S} \qquad (2)$$

where r_{diss} is the mineral dissolution rate in moles (of mineral) m^{-2}·s^{-1}, $\Delta m / \Delta t$ is calcium or phosphate release rate in mol/s, A is the total surface area of the mineral in m^2, and S is moles calcium or phosphate in the mineral. Surface areas used here are from Adcock et al. (2013).

2.5. Measurements by LIBS

LIBS measurements were performed on Mg-bearing whitlockite, Fe-bearing whitlockite, Mg-bearing merrillite, Fe-bearing merrillite, chlorapatite and fluorapatite. Mg-bearing whitlockite, Mg-bearing merrillite, and chlorapatite were synthesized, and fluorapatite purchased as described above. Fe-bearing whitlockite and Fe-bearing merrillite were synthesized as described in Adcock et al. (2014). Merrillite synthesized in this manner may contain traces of other minerals (Adcock et al., 2014).

The mineral powders (<150 μm size fraction) were pressed at 35,000 psi for 5 min to produce small pellets following a standard approach in laboratory LIBS analysis (Clegg et al., 2009; Tucker et al., 2010; Dyar et al. 2011). Samples were analyzed using the ChemCam laboratory instrument at Los Alamos, essentially identical to the one on Mars (Maurice et al., 2012; Wiens et al., 2012). Analyses were carried out at 5 m distance, under a 7 Torr CO_2 atmosphere to simulate data collection on Mars. Measurements were performed at an

TABLE 1. EXPERIMENTAL SUMMARY AND MINERAL DISSOLUTION RATES BASED ON CALCIUM AND PHOSPHATE CONCENTRATIONS OVER TIME

Experiment ID	Mineral	Organic acid	Initial pH	pH of sixth sample	r_{diss} (Ca) ($mol\cdot mineral\cdot m^{-2}\cdot s^{-1}$)	Uncertainty (Ca) ($mol\cdot mineral\cdot m^{-2}\cdot s^{-1}$)	r_{diss} (P) ($mol\cdot mineral\cdot m^{-2}\cdot s^{-1}$)	Uncertainty (P) ($mol\cdot mineral\cdot m^{-2}\cdot s^{-1}$)
ACE-MER-3	Merrillite	Acetic	5.5	5.54	7.43×10^{-9}	3.98×10^{-10}	7.39×10^{-9}	2.69×10^{-10}
ACE-MER-D-3	Merrillite	Acetic	5.5	5.54	7.87×10^{-9}	3.61×10^{-10}	7.08×10^{-9}	9.26×10^{-10}
SUC-MER-3	Merrillite	Succinic	5.5	5.56	4.86×10^{-9}	1.17×10^{-10}	7.96×10^{-9}	8.97×10^{-10}
SUC-MER-D-3	Merrillite	Succinic	5.5	5.54	5.64×10^{-9}	1.57×10^{-10}	7.78×10^{-9}	3.43×10^{-10}
MES-MER-2	Merrillite	Methylsulfonic	5.5	5.98	2.58×10^{-10}	4.58×10^{-11}	8.06×10^{-10}	6.60×10^{-11}
MES-MER-D-2	Merrillite	Methylsulfonic	5.5	5.72	3.15×10^{-10}	4.80×10^{-11}	9.41×10^{-10}	9.72×10^{-11}
DI-MER-5	Merrillite	Inorganic	5.5	4.57	8.61×10^{-10}	7.18×10^{-11}	1.06×10^{-9}	9.01×10^{-11}
DI-MER-D-5	Merrillite	Inorganic	5.5	5.47	6.21×10^{-10}	9.02×10^{-11}	1.01×10^{-9}	4.23×10^{-11}
MEL-MER-1	Merrillite	Mellitic	5.5	5.71	1.00×10^{-8}	8.45×10^{-10}	1.51×10^{-8}	3.83×10^{-10}
MEL-MER-D-1	Merrillite	Mellitic	5.5	5.61	1.07×10^{-8}	8.35×10^{-11}	1.54×10^{-8}	4.34×10^{-10}
OXA-MER-2	Merrillite	Oxalic	5.5	5.61	n.d.	n.d.	4.00×10^{-8}	4.94×10^{-9}
OXA-MER-D-2	Merrillite	Oxalic	5.5	5.65	n.d.	n.d.	3.81×10^{-8}	3.33×10^{-9}
ACE-WHIT-1	Whitlockite	Acetic	5.5	5.53	2.19×10^{-8}	6.23×10^{-9}	2.16×10^{-8}	3.22×10^{-9}
ACE-WHIT-D-1	Whitlockite	Acetic	5.5	5.54	2.31×10^{-8}	1.73×10^{-9}	2.92×10^{-8}	2.35×10^{-9}
SUC-WHIT-1	Whitlockite	Succinic	5.5	5.59	1.60×10^{-8}	3.77×10^{-10}	2.42×10^{-8}	3.79×10^{-9}
SUC-WHIT-D-1	Whitlockite	Succinic	5.5	5.58	1.58×10^{-8}	7.96×10^{-10}	2.53×10^{-8}	1.52×10^{-9}
MES-WHIT-1	Whitlockite	Methylsulfonic	5.5	6.33	1.76×10^{-9}	1.67×10^{-10}	1.00×10^{-8}	1.24×10^{-9}
MES-WHIT-D-1	Whitlockite	Methylsulfonic	5.5	6.34	1.43×10^{-9}	1.66×10^{-10}	6.55×10^{-9}	1.04×10^{-9}
DI-WHIT-1	Whitlockite	Inorganic	5.5	6.21	4.34×10^{-9}	3.21×10^{-10}	7.44×10^{-9}	1.09×10^{-9}
DI-WHIT-D-1	Whitlockite	Inorganic	5.5	6.42	5.42×10^{-9}	3.24×10^{-10}	7.49×10^{-9}	6.45×10^{-10}
MEL-WHIT-1	Whitlockite	Mellitic	5.5	5.66	2.58×10^{-8}	7.59×10^{-10}	2.18×10^{-8}	1.03×10^{-9}
MEL-WHIT-D-1	Whitlockite	Mellitic	5.5	5.60	2.29×10^{-8}	3.43×10^{-10}	1.79×10^{-8}	1.40×10^{-9}
OXA-WHIT-1	Whitlockite	Oxalic	5.5	5.84	n.d.	n.d.	5.28×10^{-8}	3.85×10^{-9}
OXA-WHIT-D-1	Whitlockite	Oxalic	5.5	5.84	n.d.	n.d.	5.37×10^{-8}	4.43×10^{-9}
ACE-CAP-2	Chlorapatite	Acetic	5.5	5.44	2.32×10^{-8}	1.35×10^{-9}	2.43×10^{-8}	2.16×10^{-9}
ACE-CAP-D-2	Chlorapatite	Acetic	5.5	5.45	2.82×10^{-8}	1.46×10^{-9}	2.52×10^{-8}	3.08×10^{-9}
SUC-CAP-1	Chlorapatite	Succinic	5.5	5.58	2.13×10^{-8}	1.41×10^{-9}	2.22×10^{-8}	3.23×10^{-9}
SUC-CAP-D-1	Chlorapatite	Succinic	5.5	5.60	2.24×10^{-8}	1.44×10^{-9}	2.49×10^{-8}	4.56×10^{-9}
MES-CAP-1	Chlorapatite	Methylsulfonic	5.5	6.90	2.46×10^{-9}	4.20×10^{-10}	1.86×10^{-9}	4.67×10^{-10}
MES-CAP-D-1	Chlorapatite	Methylsulfonic	5.5	7.10	2.39×10^{-9}	4.17×10^{-10}	1.33×10^{-9}	2.74×10^{-10}
DI-CAP-2	Chlorapatite	Inorganic	5.5	6.81	4.66×10^{-9}	3.98×10^{-10}	5.25×10^{-9}	1.58×10^{-9}
DI-CAP-D-2	Chlorapatite	Inorganic	5.5	6.81	4.83×10^{-9}	3.63×10^{-10}	6.43×10^{-9}	2.17×10^{-9}
MEL-CAP-1	Chlorapatite	Mellitic	5.5	5.64	3.86×10^{-8}	1.88×10^{-9}	2.04×10^{-8}	1.50×10^{-9}
MEL-CAP-D-1	Chlorapatite	Mellitic	5.5	5.61	3.08×10^{-8}	3.20×10^{-9}	1.81×10^{-8}	2.31×10^{-9}
OXA-CAP-1	Chlorapatite	Oxalic	5.5	5.92	n.d.	n.d.	1.06×10^{-7}	1.00×10^{-8}
OXA-CAP-D-1	Chlorapatite	Oxalic	5.5	6.00	n.d.	n.d.	8.56×10^{-8}	4.32×10^{-9}
ACE-FLAP-1	Fluorapatite	Acetic	5.5	5.52	1.56×10^{-9}	1.05×10^{-10}	2.72×10^{-9}	3.15×10^{-10}
ACE-FLAP-D-1	Fluorapatite	Acetic	5.5	5.53	1.78×10^{-9}	1.08×10^{-10}	2.53×10^{-9}	2.61×10^{-10}
SUC-FLAP-1	Fluorapatite	Succinic	5.5	5.56	2.16×10^{-9}	1.78×10^{-10}	3.92×10^{-9}	5.08×10^{-10}
SUC-FLAP-D-1	Fluorapatite	Succinic	5.5	5.58	2.44×10^{-9}	2.68×10^{-10}	4.06×10^{-9}	2.72×10^{-10}
MES-FLAP-1	Fluorapatite	Methylsulfonic	5.5	4.90	7.23×10^{-10}	1.97×10^{-10}	1.88×10^{-9}	1.92×10^{-10}
MES-FLAP-D-1	Fluorapatite	Methylsulfonic	5.5	4.80	6.44×10^{-10}	7.05×10^{-11}	1.98×10^{-9}	3.54×10^{-10}
DI-FLAP-1	Fluorapatite	Inorganic	5.5	4.76	1.34×10^{-9}	2.19×10^{-10}	2.11×10^{-9}	3.83×10^{-10}
DI-FLAP-D-1	Fluorapatite	Inorganic	5.5	4.76	1.28×10^{-9}	7.03×10^{-11}	1.65×10^{-9}	2.47×10^{-10}
MEL-FLAP-1	Fluorapatite	Mellitic	5.5	5.65	6.11×10^{-9}	4.91×10^{-10}	7.34×10^{-9}	4.83×10^{-10}
MEL-FLAP-D-1	Fluorapatite	Mellitic	5.5	5.62	5.11×10^{-9}	6.93×10^{-10}	6.77×10^{-9}	5.51×10^{-10}
OXA-FLAP-1	Fluorapatite	Oxalic	5.5	5.50	n.d.	n.d.	8.38×10^{-8}	2.27×10^{-9}
OXA-FLAP-D-1	Fluorapatite	Oxalic	5.5	5.51	n.d.	n.d.	8.58×10^{-8}	4.23×10^{-9}

instrument temperature of 13.2°C, with 1 titanium standard analyzed to verify proper wavelength calibration. Each measurement consisted of 50 laser shots at 14 mJ a rate of 3 Hz, in five different locations on each pellet. The mean of the 50 shots was used for all analyses.

3. Results

3.1. pH change

Overall, pH values for the dissolution experiments increased to the largest extent during the six time points used for calculating dissolution rates (Table 1) for inorganic solutions and solutions containing methylsulfonic acid (with the greatest increase up to ∼pH = 7). pH changes in oxalic acid-containing solutions showed the second largest increase (up to pH = 6.00), and all other solutions showed relatively little increase (up to pH = 5.71) (see also Table 1). This difference is most likely due to the buffering effect of the weak organic acids relative to methylsulfonic acid, which is a strong acid, and the inorganic solutions, which

contained no organic acids. The increase in pH in the oxalic acid solutions is most likely due to large amounts of dissolution occurring in those solutions (Table 1).

3.2. Ca and P release

Phosphate release and calcium release, where calcium was measurable, were both linear over the first six sampling points used for calculating dissolution rates (Figs. 1 and 2 and SOM). Calcium was not measurable in the presence of oxalic acid likely due to the precipitation of calcium oxalate (Goyne *et al.*, 2006). For all minerals, phosphate release rates were greatest in the presence of oxalic acid (as much as 45× the inorganic control). Phosphate release rates from whitlockite, merrillite and chlorapatite were enhanced relative to the inorganic control (2.5 to >35×) for all organic compounds except methylsulfonic acid. In contrast, phosphate release rates from fluorapatite showed little effect from acetic, methylsulfonic and succinic acids (up to ≈2× release rates from the inorganic control). Calcium release
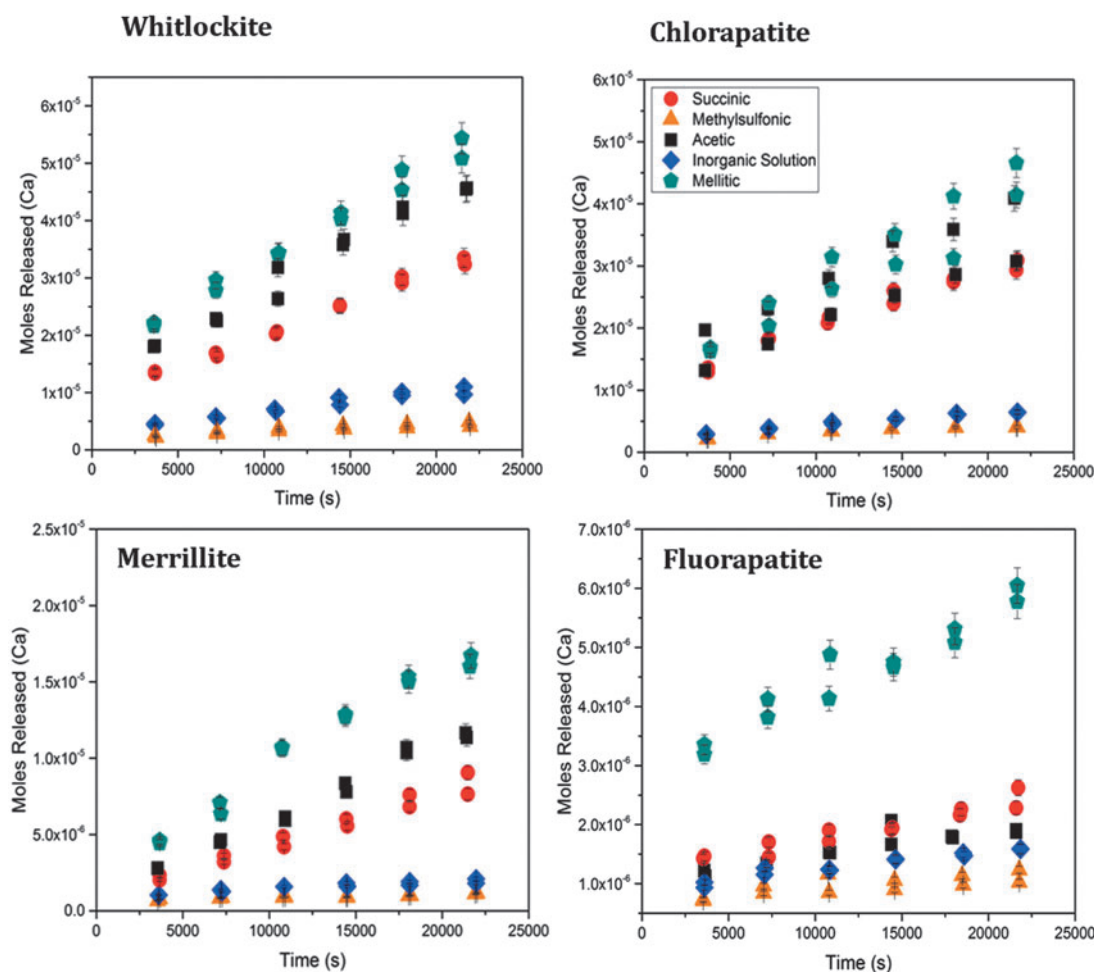
FIG. 1. Calcium release from each mineral in the presence of the organic compounds. Mellitic acid caused a consistently large dissolution enhancement from all four minerals relative to inorganic solutions. Acetic acid and succinic acid resulted in a large enhancement of whitlockite, merrillite, and chlorapatite dissolution relative to inorganic solutions. However, in the presence of acetic acid and succinic acid, dissolution of fluorapatite was not significantly enhanced relative to the experiments containing inorganic solutions, which we attribute to the fact that fluorapatite dissolution occurs farther from equilibrium. Error bars represent analytical uncertainty estimated as 5% (APHA, 2005). Note differences in scale on the *y*-axis to accommodate different concentrations.
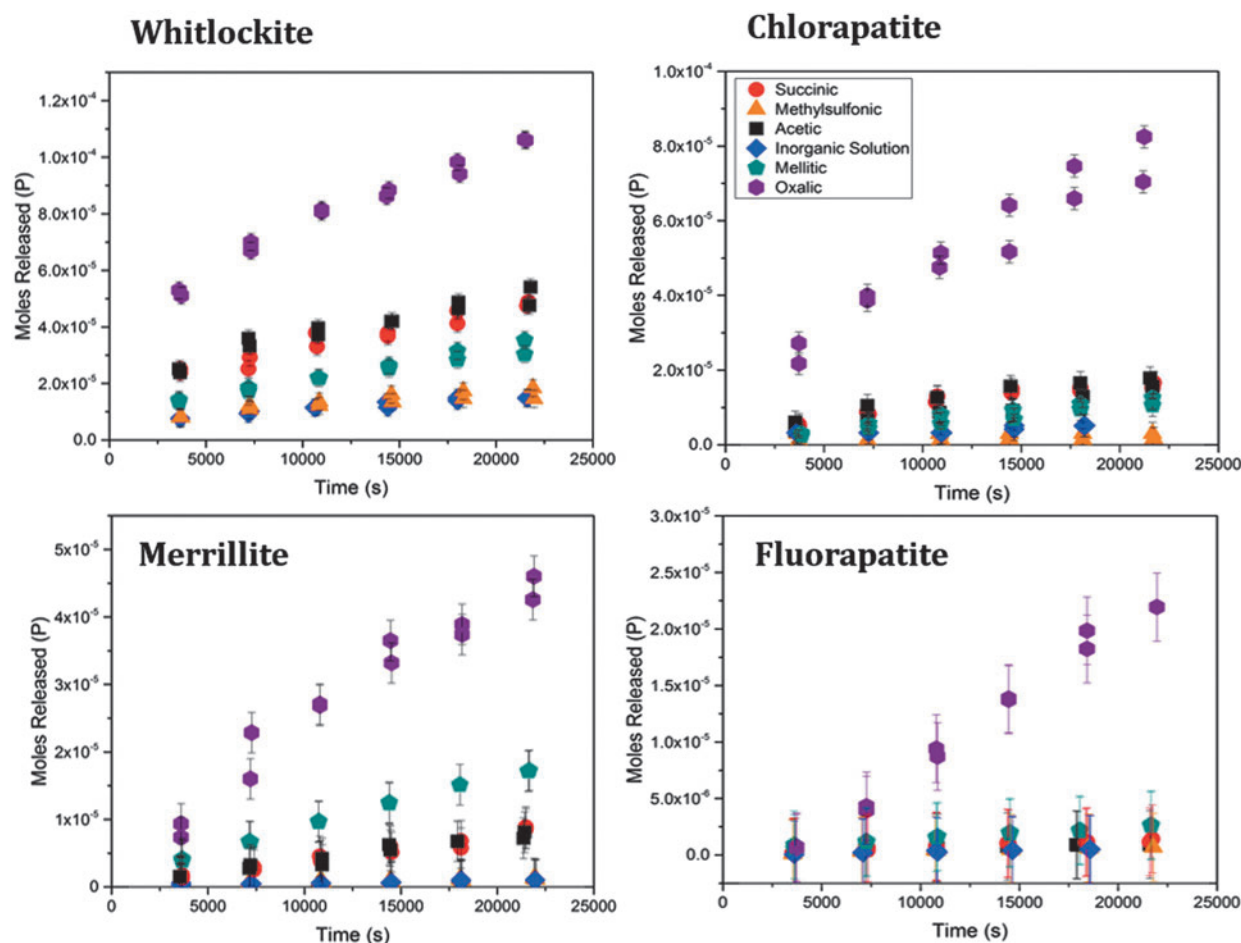
FIG. 2. Phosphate release in the presence of the organic acids. Oxalic acid has the greatest effect on phosphate release from all four minerals, likely due to its behavior as a bidentate ligand. Phosphate release from whitlockite, merrillite and chlorapatite is more significantly enhanced relative to inorganic solutions in the presence of acetic and succinic acid than fluorapatite, which we attribute to the fact that fluorapatite dissolution occurs farther from equilibrium. Error bars represent analytical uncertainty of 0.003 m*M*, based on the average of the standard error of the calibration. Note different scales on the *y*-axis to accommodate different concentrations.

rates were enhanced from whitlockite, merrillite, and chlorapatite in the presence of all organic compounds relative to the inorganic control (3 to $\approx 14\times$) except methylsulfonic acid, with mellitic acid generally having the largest effect (≈ 5 to $\approx 14\times$). Fluorapatite showed a strong enhancement of Ca release rates relative to the inorganic control only in the presence of mellitic acid (>4$\times$ the inorganic control). Elemental release trends in specific organic acid solutions are discussed further in the Discussion section.

3.3. Stoichiometry

Calcium and phosphate concentrations in solution were compared to the stoichiometric Ca:P ratio in each mineral. The Ca:P ratios for chlorapatite $Ca_5(PO_4)_3Cl$, whitlockite $Ca_9Mg(PO_3OH)(PO_4)_6$, and fluorapatite $Ca_5(PO_4)_3F$ used in this study are based on the International Mineralogical Association (IMA) formulae. The Ca:P ratio in merrillite [$Ca_{9.5}Mg(PO_4)_7$] is based on a previous study by Adcock *et al.* (2013), which used electron probe micro-analysis to confirm calcium substitution in synthesized merrillite.

All minerals showed non-stochiometric dissolution, with merrillite and fluorapatite showing Ca:P ratios that are

closest to stoichiometric release (Fig. 3). Whitlockite showed decreased Ca:P ratios for all organic compounds except mellitic acid, while chlorapatite showed increased Ca:P ratios for all organic compounds (Fig. 3).

Previous studies of fluorapatite dissolution have shown the initial release of calcium to be greater than the release of other elements such as phosphate or fluorine, with longer term release (up to 2 months) reaching ratios that are closer to stoichiometric ratios (Valsami-Jones *et al.*, 1998; Welch *et al.*, 2002; Guidry and Mackenzie, 2003; Chairat *et al.*, 2007). Enhanced calcium release relative to other ions present in phosphate minerals is potentially due to the preferential leaching of calcium from the phosphate mineral surface (Valsami-Jones *et al.*, 1998). Phosphate is released from the calcium-depleted mineral surface layer, resulting in a Ca:P ratio that ultimately trends toward stoichiometric dissolution over time. In addition to the possible formation of a cation-depleted surface layer, re-adsorption of calcium onto the mineral surface could cause non-stoichiometric dissolution (Guidry and Mackenzie, 2003; Goyne *et al.*, 2006). The Ca:P ratios measured here indicate that both processes may be occurring in our experiments.
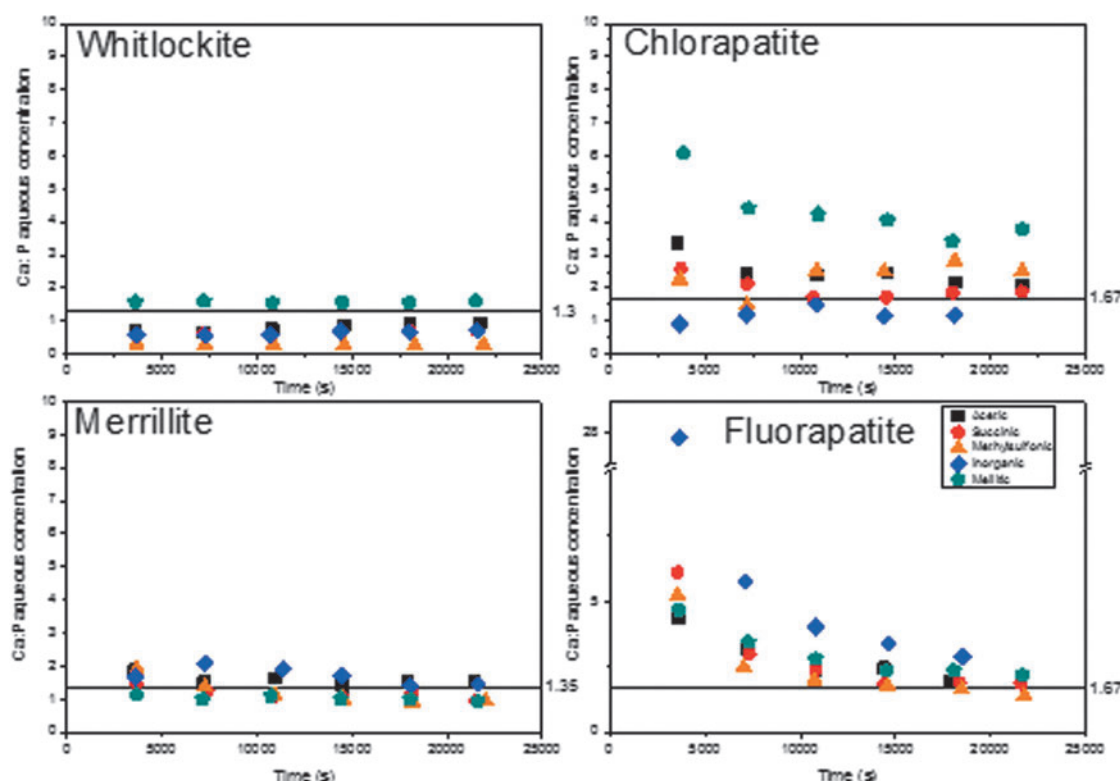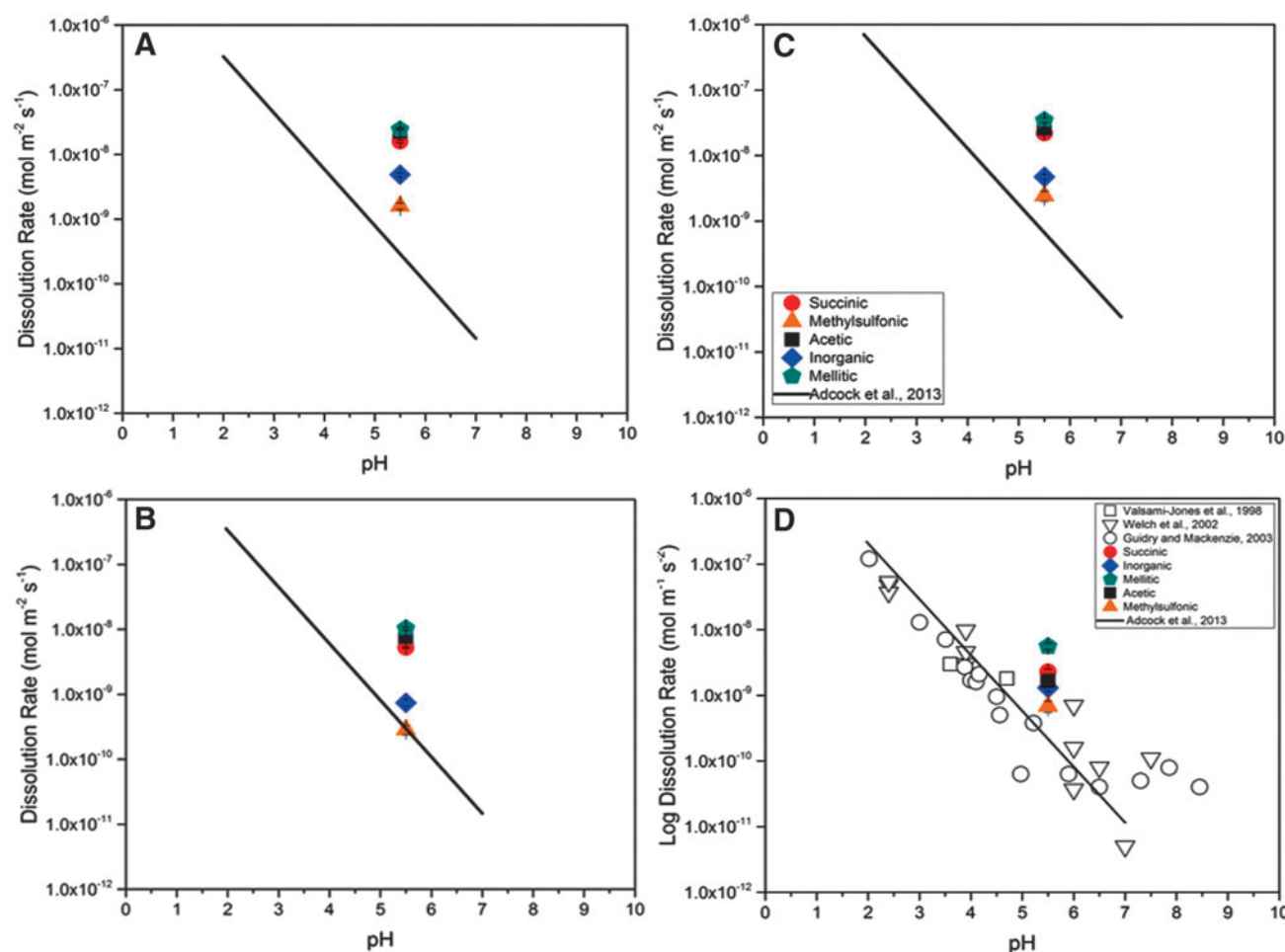
FIG. 4. Mineral dissolution rates measured in this study of **(A)** whitlockite, **(B)** merrillite, **(C)** chlorapatite, and **(D)** fluorapatite in the presence of mellitic, acetic, succinic, and methylsulfonic acids, and inorganic solutions compared to previous data from the literature. Previous studies were performed at 22–25°C and in inorganic solutions (Valsami-Jones *et al.*, 1998; Welch *et al.*, 2002; Guidry and Mackenzie, 2003; Adcock *et al.*, 2013). Colored points indicate dissolution rates measured in this study, black outlines indicate dissolution rates previously measured, and lines indicate dissolution rate laws from Adcock *et al.* (2013). Error bars indicate the standard error of the rate. Color graphics are available at www.liebertonline.com/ast.

at Los Alamos National Laboratory to determine if they can be distinguished by LIBS analyses. Below we discuss our results and their implications for Mars.

Organic compounds have been previously found to enhance mineral dissolution by three mechanisms: (1) de-

TABLE 2. SATURATION INDICES OF THE SOLUTIONS
FOR THE FIRST AND SIXTH TIME POINT OF EACH
INORGANIC EXPERIMENT WITH RESPECT
TO DI-CALCIUM PHOSPHATE ANHYDROUS

Mineral	SI with respect to DCPA (first concentration)	SI with respect to DCPA (sixth concentration)
Fluorapatite	−7.39	−6.39
Merrillite	−5.91	−5.08
Whitlockite	−3.45	−2.68
Chlorapatite	−5.75	−4.72

Solutions from fluorapatite dissolution experiments are more undersaturated with respect to DCPA than other minerals tested.
DCPA, di-calcium phosphate anhydrous; SI, saturation index.

creasing the pH of the solution, which can enhance dissolution (*e.g.*, Tan, 1986; Furrer and Stumm, 1986); (2) forming complexes at the mineral surface that enhance dissolution (*e.g.*, Furrer and Stumm, 1986; Stumm, 1997; Olsen and Rimstidt, 2008); and (3) enhancing dissolution by complexing ions in solution and therefore changing the extent of saturation of the solution with respect to a solid phase (*e.g.*, Drever and Stillings, 1997). Our solutions were initially pH-controlled, and consequently we do not anticipate significant differences in mineral dissolution rates due to changes in pH. Dissolution in organic-containing solutions in our experiments is likely enhanced relative to inorganic controls both by complex formation at the mineral surface and by complexation of ions in solution changing the solution saturation state.

Oxalic acid-bearing solutions resulted in the largest increase in phosphate release rates relative to inorganic controls for all minerals. Calcium release in the presence of oxalic acid solutions could not be measured due to the presumed formation of calcium oxalate, as has been previously documented (Goyne *et al.*, 2006). Oxalate has two
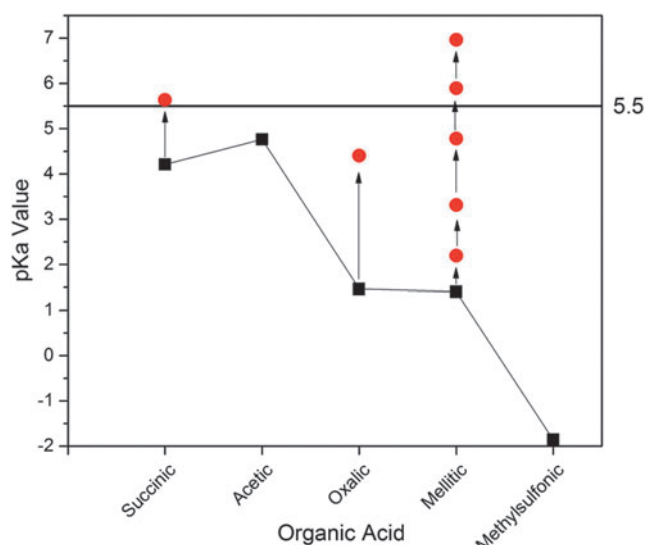
FIG. 5. Dissociation constants for each organic acid used in this study. Black squares represent the pK$_a$ value corresponding to the first proton loss, red circles represent the pK$_a$ values for additional proton loss. The horizontal line at 5.5 indicates the experimental pH. All organic compounds are fully dissociated except for succinic and mellitic acid. Color graphics are available at www.liebertonline.com/ast.

carboxyl groups, both of which are fully deprotonated at the pH of our experiments ($\sim$5.5) (Fig. 5), and oxalate can function as a bidentate ligand (Valsami-Jones *et al.*, 1998; Neaman *et al.*, 2005). Previous work by Furrer and Stumm (1986) found that bidentate ligands can enhance dissolution by ion complexation at the mineral surface, a process that they did not observe for monodentate ligands. Other work has also found that five membered chelate rings, such as the oxalate ion, are particularly effective at enhancing dissolution (Furrer and Stumm, 1986; Neaman *et al.*, 2005; Goyne *et al.*, 2006). Enhancement of elemental release by oxalate has been shown at concentrations as low as micromolar to millimolar (Goyne *et al.*, 2006; Olsen and Rimstidt, 2008), and previous work has also shown that the relationship between the log dissolution rate and the log concentration of oxalic acid is linear (Olsen and Rimstidt, 2008).

Mellitic acid in solution shows, in general, the largest enhancement of calcium release rates relative to inorganic solutions (4 to $\sim$14$\times$ release rates from the inorganic control). Mellitic acid has the largest number of deprotonated carboxyl groups used in our experiments, with four per molecule at pH 5.5. Previous work by Wu *et al.* (1996) suggests multiple bonding possibilities for mellitic acid, including its ability to act as a bidentate ligand, chain formation, and monodentate complexation. Mellitic acid may therefore be capable of enhancing dissolution by complexation at the mineral surface as a bidentate ligand.

In contrast to oxalic and mellitic acids, both succinic and acetic acid are monodentate ligands at the pH of our experiments. Based on previous work (Furrer and Stumm, 1986), we therefore would not expect them to significantly enhance dissolution rates by forming complexes at the mineral surface. Perhaps due in part to diminished surface complexation, our experiments show that calcium release

rates from fluorapatite are minimally enhanced by acetic acid and succinic acid relative to the inorganic controls (<2$\times$ Ca release rates from the inorganic control). These observations are consistent with previous work on fluorapatite dissolution in the presence of acetic and succinic acid (Neaman *et al.*, 2005; Goyne *et al.*, 2006). However, surprisingly, our experiments show that acetic acid and succinic acid substantially enhance (3 to 10$\times$) calcium release rates from whitlockite, merrillite, and chlorapatite relative to calcium release rates from the inorganic mineral control (Table 1). We therefore examine whether this effect could be due to changes in extent of undersaturation relative to the solid phase as previously observed by Drever and Stillings (1997) for mineral dissolution in the presence of organic compounds.

Previous work has found that fluorapatite forms a leached surface layer during dissolution experiments that controls the apparent solubility of the mineral (Chairat *et al.*, 2007). Making the assumption that such a leached layer might also form on other calcium phosphate minerals during dissolution, we calculated the SI for the first and sixth time point (final time point used in calculation of dissolution rates) of each of our inorganic experiments with respect to DCPA, the mineral present in the previously studied leached layer (Chairat *et al.*, 2007) to test whether the extent of undersaturation might be affecting dissolution rates in our experiments. Our results (Table 2) show that the solutions present in the fluorapatite dissolution experiments are most undersaturated with respect to DCPA, while solutions in the chlorapatite, whitlockite, and merrillite experiments are closer to equilibrium with DCPA. Chlorapatite, whitlockite, and merrillite dissolution may therefore be occurring closer to equilibrium with this putative leached layer, due to the faster inorganic dissolution rates of these minerals.

We therefore hypothesize that in the solutions that are closer to equilibrium (in the whitlockite, merrillite and chlorapatite experiments), the presence of organic compounds that can complex Ca in solution changes the solution saturation state sufficiently to enhance dissolution. In contrast, for fluorapatite dissolution, we hypothesize that since dissolution is occurring farther from equilibrium, changing the solution saturation state with the monodentate acetic and succinic acids results in little change in dissolution rates relative to the inorganic controls. To test this hypothesis, we examine the ligand-cation complex for each ligand.

The ligand-cation stability constant has been previously used to explain differences in elemental release during dissolution in the presence of organic acid (Hausrath *et al.*, 2009). However, stability constants with Ca and Mg have not been measured for all the organic compounds used in this study. The strength of the ligand-cation complex is, however, correlated with the compound's pK$_a$ (Dimmock *et al.*, 1995). We therefore compare dissolution rate enhancement in the presence of each organic compound relative to the inorganic control to the pK$_a$ value for each acid (Fig. 6 and Table 3). The pK$_a$ of the organic compound is a good predictor of the extent of dissolution enhancement in the presence of the organic compound relative to the inorganic control from chlorapatite, whitlockite, and merrillite where we expect ligand-Ca complexation in solution to play an important role in dissolution enhancement due to solutions that are closer to equilibrium (Fig. 6). Fluorapatite
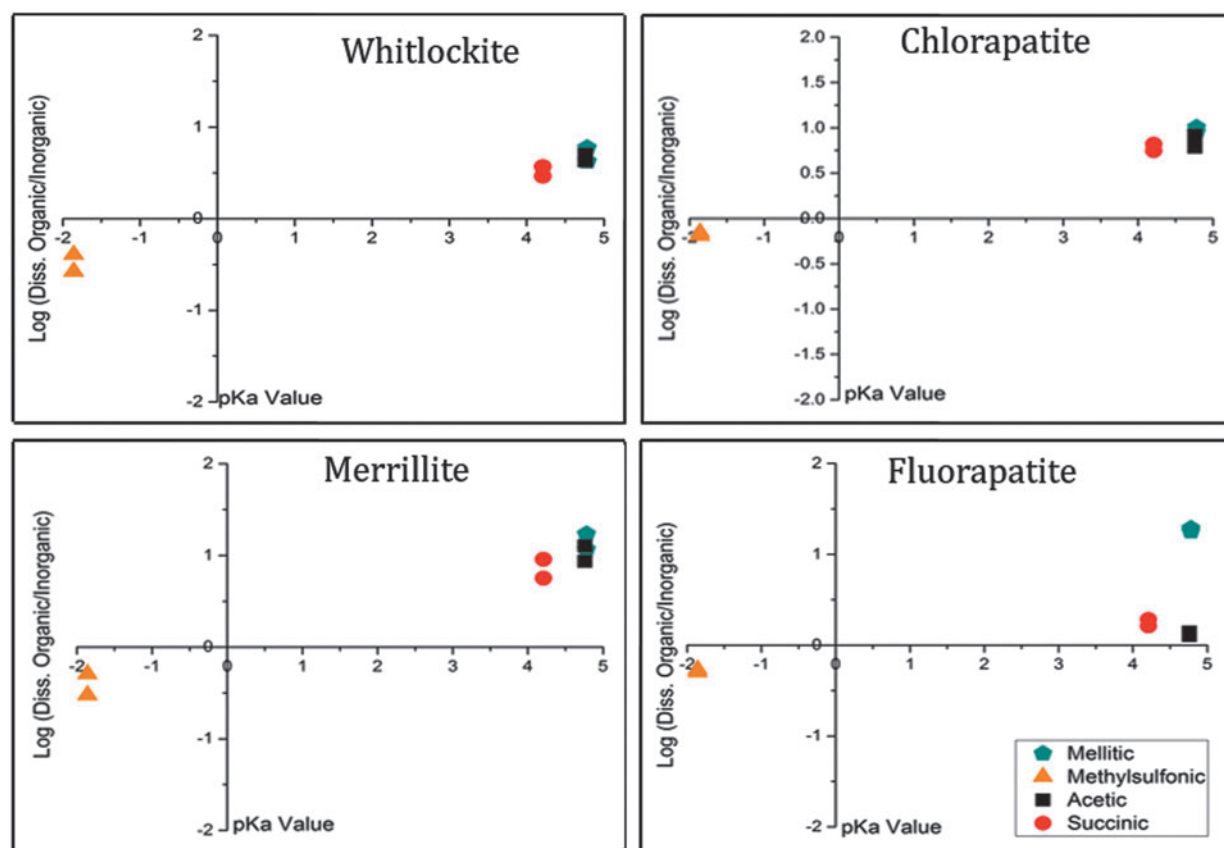
FIG. 6. The log of the ratio of the mineral dissolution rate in the presence of the organic compound to the inorganic dissolution rate (based on calcium) versus the pK_a for each organic acid. These results indicate that the lack of enhancement of dissolution in the presence of methylsulfonic acid relative to inorganic controls is consistent with its characteristic as a strong acid, and that the pK_a is a reasonable predictor for enhanced calcium release from whitlockite, merrillite and chlorapatite relative to inorganic solutions. The trend does not hold for fluorapatite, which is likely due to a greater extent of undersaturation as discussed in section 4: Discussion.

dissolution breaks from this trend, however, supporting the conclusion that aqueous ligand-Ca complexation is less important to dissolution of fluorapatite due to the greater extent of undersaturation in solutions relative to the leached layer solid phase (Fig. 6).

Ca and P release rates in the presence of methylsulfonic acid were either slightly decreased relative to, or similar to, the inorganic controls ($0.27–1.11\times$ release rates from the inorganic controls) (Table 1). The lack of dissolution enhancement relative to inorganic controls is consistent with the fact that methylsulfonic acid is a strong acid, and therefore not expected to bind strongly to the calcium ion (Fig. 6). We also anticipate that traces of sulfate or sulfite contamination in the methylsulfonic acid may be forming an armoring layer on the mineral surface and decreasing dissolution based on previous observations of sulfite as a breakdown product of methylsulfonic acid (Thompson *et al.*, 1995) (Fig. 6).
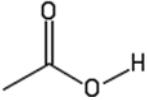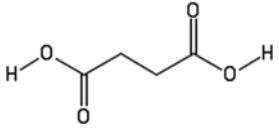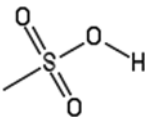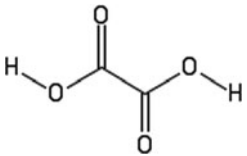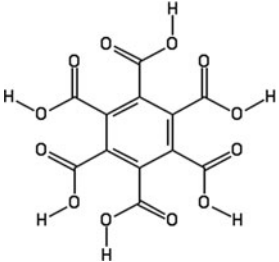
In summary, we propose that the largest enhancement in elemental release rates shown for oxalic ($7–45\times$) and mellitic acid (~ 2.5 to $14\times$ release rates from inorganic controls) is due to the fact that these ligands can behave as bidentate ligands, and thus complex ions both at the mineral surface and in solution. In contrast, we anticipate that acetic and succinic acids, which are monodentate at the pH of our experiments, affect dissolution primarily through aqueous ion

complexation which changes the extent of undersaturation with respect to the solid phase. The impact of acetic and succinic acids is much greater on whitlockite, merrillite and chlorapatite dissolution rates ($3–10\times$ dissolution rates of inorganic controls), where solutions are closer to equilibrium with DCPA, than on fluorapatite dissolution rates ($<\sim 2\times$ inorganic controls), which are farther from equilibrium with DCPA. Consistent with this hypothesis, the pK_as of each compound, which are correlated with the strength of the ligand-cation complex (Dimmock *et al.*, 1995), are good predictors of dissolution enhancement of chlorapatite, whitlockite, and merrillite, but not fluorapatite. Methylsulfonic acid, a strong acid, shows either a slight decrease to no effect ($0.27–1.11\times$ release rates from the inorganic controls).

4.1. Implications for Mars

Multiple phosphates, including F-rich apatite (McCubbin and Nekvasil, 2008), Cl-rich apatite (McSween and Treiman, 1998; Bridges and Grady, 2000; Greenwood *et al.*, 2003), and merrillite (McSween and Treiman, 1998; Greenwood *et al.*, 2003; Shearer *et al.*, 2015) are present in martian meteorites. In addition, apparent depletion of phosphate and formation of secondary phosphate phases suggests aqueous alteration of calcium phosphate minerals on Mars (Hurowitz *et al.*, 2006;

TABLE 3. CHEMICAL FORMULAE, STRUCTURES, AND pK$_A$ VALUES FOR ORGANIC ACIDS USED IN THIS STUDY

Organic acid	Chemical formula	Structure	pK$_a$	Denticity under experimental conditions
Acetic acid	$C_2H_4O_2$		4.76	Monodentate
Succinic acid	$C_4H_6O_4$		4.21, 5.72	Monodentate
Methylsulfonic acid	CH_4O_3S		−1.86	Monodentate
Oxalic acid	$C_2H_2O_4$		1.46, 4.40	Bidentate
Mellitic acid	$C_{12}H_6O_{12}$		1.40, 2.19, 3.31, 4.78, 5.89, 6.96	Monodentate, bidentate

All pK$_a$ values obtained from Martell and Smith (1974).

Lane *et al.*, 2008; Hausrath *et al.*, 2013; Adcock and Hausrath, 2015; Berger *et al.*, 2016; Forni *et al.*, 2017). Multiple instruments, including Alpha Particle X-ray Spectrometer (APXS), CheMin, Mössbauer, and SHERLOC, have been used on the Mars Exploration Rovers and Mars Science Laboratory (MSL) rover, or can be used (Mars 2020), to examine phosphate minerals and mobility on Mars (*e.g.*, Hurowitz *et al.*, 2006; Lane *et al.*, 2008; Ming *et al.*, 2008; Hausrath *et al.*, 2013; Beegle *et al.*, 2014; Rampe *et al.*, 2017).

LIBS measurements of these Mars-relevant phosphate minerals indicate that they can potentially be distinguished from each other using the ChemCam or SuperCam instrument on Mars. Specifically, fluorapatite can be distinguished by the CaF peak (SOM) and either the presence of P or the amount of F present to distinguish it from fluorite as has previously been demonstrated by Forni *et al.* (2015); Meslin *et al.* (2016); Forni *et al.* (2017), and chlorapatite can be similarly distinguished using the CaCl peak (SOM). Furthermore, both Mg- and Fe-bearing whitlockite can be distinguished from Mg- and Fe-bearing merrillite by the presence or absence of the H peak in LIBS data, respectively (SOM). The ability to

identify these minerals on Mars will also be strengthened by the presence of the Raman on SuperCam, as well as the chemical analyses present from PIXL on Mars 2020. The potential identification of these minerals *in situ*, with their different dissolution behavior under both inorganic and organic conditions, has the ability to help interpret phosphate mobility on Mars, as well as a better understanding of martian phosphate minerals (Adcock *et al.*, 2017).

Phosphate release rates from chlorapatite, whitlockite, and merrillite were enhanced by mellitic, oxalic, succinic, and acetic acids by as much as >35× relative to inorganic controls. Importantly, dissolution rates of merrillite, whitlockite, and chlorapatite were much more strongly enhanced by acetic and succinic acids (3–10× dissolution rates of inorganic controls) than were dissolution rates of fluorapatite (<~2× dissolution rates of inorganic controls). This may be due to the fact that dissolution of whitlockite, merrillite, and chlorapatite is likely occurring much closer to equilibrium with a leached layer, suggesting that these minerals might be more sensitive indicators of the presence of organic compounds than fluorapatite.

This difference in the effect of the organic compounds on different phosphate minerals is important to understanding Mars. While F and Cl contents of apatite on Mars vary broadly and fluorapatite or F-rich apatite has been found in martian meteorites (*e.g.*, McCubbin and Nekvasil, 2008; McCubbin *et al.*, 2016) and detected at Gale Crater on Mars (Forni *et al.*, 2015; Treiman *et al.*, 2016), and the dominant terrestrial igneous phosphate mineral is fluorapatite (*e.g.*, McKelvey, 1973; McClellan and Van Kauwenbergh, 1990), meteorites suggest that chlorapatite or Cl-rich apatite is more prevalent on Mars than Earth (McCubbin *et al.*, 2016). In fact, the most representative sample of the martian crust and surface, the 4.4 Ga regolith breccia meteorite Northwest Africa (NWA) 7034 and paired meteorites (Agee *et al.*, 2013; Hewins *et al.*, 2013; Udry *et al.*, 2014; Santos *et al.*, 2015), contains almost exclusively chlorapatite (*i.e.*, >50% Cl^- occupancy of the F,Cl,OH site) (McCubbin *et al.*, 2016). Thus, chlorapatite was likely an important phosphate phase on Mars during the Noachian. Moreover, merrillite is the dominant phosphate species in some martian meteorites such as the shergottites (McSween and Treiman, 1998; Shearer *et al.*, 2011, 2015; McCubbin *et al.*, 2016; Adcock *et al.*, 2017). Understanding the different dissolution behavior of these Mars-relevant minerals is therefore important for understanding past water-rock interactions on Mars.

The effect of organic compounds on phosphate mineral depletion has previously been documented in terrestrial paleosols, where it has been interpreted as evidence of ligands secreted by terrestrial organisms (Neaman *et al.*, 2005). Similar results showing phosphate depletion from basalts in the presence of organic acids in laboratory experiments (Hausrath *et al.*, 2009) and in modern soils (Hausrath *et al.*, 2011) have also been documented. Our results showing that Mars-relevant phosphate minerals can be more sensitive to organic compounds than fluorapatite therefore indicate that preferential depletion of phosphate minerals on Mars would be a more sensitive indicator of the presence of organic compounds, whether biotic or deposited from meteorites, than on Earth.

Observations that would confirm the past presence of organic compounds on Mars may be difficult. Neaman *et al.* (2005) argued that mobilization of Fe and P, but immobility of Al, was consistent with the presence of organic compounds under low water conditions, thereby allowing the mobility of Fe and P to be attributed to organic compounds rather than simply leaching. Although such observations would always need to be taken into context and examined in light of all data, in a similarly developed weathering profile or paleosol on Mars, mobilization of Fe and P, but immobility of Al might similarly indicate the presence of past organic compounds.

Recent data from the SAM instrument have indicated the presence of perchlorate, benzoic acid, dichloroalkanes and chlorobenzenes (Freissinet *et al.*, 2015; Miller *et al.*, 2016), as well as potential precursors of chlorobenzene formation such as propanol, 1,2-dichloropropane, and benzene carboxylic acids (Miller *et al.*, 2016), and pyrolysis products including thiophenic, aromatic, and aliphatic compounds at high temperatures (Eigenbrode *et al.*, 2018). Estimates suggest that the concentrations of benzenhexacarboxylic acid (mellitic acid) present in martian soils may have been as high as 500 ppm organic carbon (500 mg mellitic acid per kg soil) in the top meter of martian soil after 3 billion years

(Benner *et al.*, 2000). Measurements by SAM indicate values in Yellowknife Bay of up to about 300 ppb (Freissinet *et al.*, 2015), and nanomolar concentrations in Mojave and Confidence Hills (Eigenbrode *et al.*, 2018).

Meteorite-deposited organic matter might have been important on early Mars during the Noachian, when there may have been more abundant water than currently present on Mars. Mellitic and oxalic acids generated as postulated by Benner *et al.* (2000) could also have impacted dissolution in episodic water present in the Hesperian and Amazonian. However, a putative martian biosphere might have produced much more abundant organic acids than those deposited from meteorites, and acetic, succinic, and oxalic acids are known to be produced by terrestrial microorganisms (Heyer and Krumbein, 1991; Prescott *et al.*, 1996; Madigan *et al.*, 2003). Therefore, the presence of such a martian biosphere might well be recorded in the sensitivity of merrillite, chlorapatite and whitlockite dissolution to the presence of organic acids. This potential organomarker should be tested against other potential biosignatures (*e.g.*, Hays *et al.*, 2017), particularly since clay minerals that can preserve organic compounds can also record oxidized conditions that may destroy them (Gainey *et al.*, 2017).

Increases in phosphate release from Mars-relevant minerals due to organic compounds might have been even more pronounced at the higher and potentially more habitable circumneutral pH values found at Gale Crater (Grotzinger *et al.*, 2014) and the Phoenix landing site (Kounaves *et al.*, 2010). Greater deprotonation at higher pH values above the pK_as of organic acids would provide more reactive, negatively charged ligands to react with phosphate minerals and complex aqueous cations. The observed effect of organic compounds on martian phosphate dissolution would therefore have been strongest under near-neutral, habitable conditions.

5. Conclusions

This study provides evidence that a range of organic compounds likely present in martian soils can enhance phosphate release from Mars-relevant minerals relative to dissolution in inorganic solutions. Specifically, dissolution of Mars-relevant merrillite, whitlockite, and chlorapatite was much more strongly enhanced by acetic and succinic acids than was fluorapatite, the dominant terrestrial igneous phosphate mineral. Acetic and succinic acid are likely present on Mars from carbonaceous chondrites, and they are also produced by terrestrial microorganisms (Heyer and Krumbein, 1991; Prescott *et al.*, 1996; Madigan *et al.*, 2003).

Phosphate mobility from paleosols has been considered a proxy for organic compounds secreted by terrestrial organisms on early Earth (Neaman *et al.*, 2005). Importantly, our results suggest that dissolution of the dominant phosphate minerals on Mars may be strongly impacted by organic compounds, making depletion of these phosphate-bearing minerals a potentially sensitive indicator of the past presence of organic compounds on Mars. We also show that the minerals tested here can be distinguished from each other by ChemCam, and also SuperCam LIBS which is being developed for the Mars 2020 rover. Further work is needed to understand the behavior of these Mars-relevant minerals in the presence of a wide range of potential biotic and prebiotic organic compounds.

Acknowledgments

Author Disclosure Statement

No competing financial interests exist.

References

Adcock, C.T. and Hausrath, E.M. (2015) Weathering profiles in high-P rocks at Gusev Crater, Mars, suggest dissolution of phosphate minerals into near-neutral waters *Astrobiology* 15: 1060–1075.

Adcock, C.T., Hausrath, E.M., and Forster, P.M. (2013) Readily available phosphate from minerals in early aqueous environments on Mars. *Nat Geosci* 6:824–827.

Adcock, C.T., Hausrath, E.M., Forster, P.M., and Sefein, K.J. (2014) Synthesis and characterization of the Mars-relevant phosphate minerals Fe/Mg-whitlockite and merrillite and a proposed mechanism for whitlockite to merrillite transformation. *Am Mineral* 99:1221–1232.

Adcock, C.T., Tschauner, O., Hausrath, E.M., Udry, A., Luo, S.N., Ren, M., Cai, Y., Lanzirotti, A., Newville, M., Kunz, M., and Lin, C. (2017) Shock-transformation of whitlockite to merrillite and the implications for meteoritic phosphate. *Nat Commun* 8:14667.

Agee, C.B., Wilson, N.V., McCubbin, F.M., Ziegler, K., Polyak, V.J., Sharp, Z.D., Asmerom, Y., Nunn, M.H., Shaheen, R., Thiemens, M.H., Steele, A., Fogel, M.L., Bowden, R., Glamoclija, M., Zhang, Z., and Elardo, S.M. (2013) Unique meteorite from early Amazonian Mars: water-rich basaltic breccia Northwest Africa 7034. *Science* 339:780–785.

APHA. (2005) *Standard Methods for the Examination of Water and Waste Water*, 21st ed., American Public Health Association, Washington, DC.

Beegle, L.W., Bhartia, R., DeFlores, L.P., Darrach, M., Kidd, R.D., Abbey, W., Asher, S., Burton, A., Clegg, S., Conrad. P.G., Edgett, K., Ehlmann, B., Hug, W., Langenhorst, F., Fries, M., Nealson, K., Popp, J., Sobron, P., Steele, A., Wiens, R., and Williford, K. (2014) SHERLOC: scanning habitable environments with Raman and luminescence for organics and chemicals, an investigation for 2020. *LPSC* Abstract #2835. Lunar Planetary Institute, Houston.

Benner, S.A., Devine, K.G., Matveeva, L.N., and Powell, D.H. (2000) The missing organic molecules on Mars. *Proc Natl Aacd Sci U S A* 97:2425–2430.

Berger, J.A., Schmidt, M.E., Izawa, M.R.M., Gellert, R., Ming, D.W., Rampe, E.B., VanBommel, S.J., and McAdam, A.C. (2016) Phosphate stability in diagenetic fluids constrains the acidic alteration model for lower Mt. Sharp sedimentary rocks in Gale Crater, Mars [abstract 1652]. In *47th Lunar and Planetary Science Conference*, Lunar and Planetary Institute, Houston.

Bridges, J.C. and Grady, M.M. (2000) Evaporite mineral assemblages in the nakhlite (martian) meteorites. *Earth Planet Sci Lett* 176:267–279.

Chairat, C., Schott, J., Oelkers, E.H., Lartigue, J.E., and Harouiya, N. (2007) Kinetics and mechanism of natural fluorapatite dissolution at 25 C and pH from 3 to 12. *Geochim Cosmochim Acta* 71:5901–5912.

Clegg, S., Sklute, E., Dyar, M., Barefield, J., and Wiens, R. (2009) Multivariate analysis of remote laser-induced breakdown spectroscopy spectra using partial least squares, principal component analysis, and related techniques. *Spectrochim Acta Part B At Spectrosc* 64:79–88.

Cooper, G.W., Onwo, W.M., and Cronin, J.R. (1992) Alkyl phosphonic acids and sulfonic acids in the Murchison meteorite. *Geochim Cosmochim Acta* 56:4109–4115.

Dachs, E., Harlov, D., and Benisek, A. (2010) Excess heat capacity and entropy of mixing along the chlorapatite-fluorapatite binary join. *Phys Chem Miner* 37:665–676.

Derenne, S. and Robert, F. (2010) Model of molecular structure of the insoluble organic matter isolated from Murchison meteorite. *Meteorit Planet Sci* 45:1461–1475.

Dimmock, P.W., Warwick, P., and Robbins, R.A. (1995) Tutorial review: approaches to predicting stability constants. *Analyst* 120:2159–2170.

Drever, J.I. and Stillings, L.L. (1997) The role of organic acids in mineral weathering. *Colloid Surf A Physicochem Eng Asp* 120:167–181.

Dyar, M.D., Carmosino, M.L., Tucker, J.M., Speicher, E.A., Brown, E.B., Clegg, S.M., Wiens, R.C., Barefield, J.E., Delaney, J.S., Ashley, G.M., and Driese, S.G. (2011) Error analysis for remote laser-induced breakdown spectroscopy analysis using combinations of igneous sedimentary and phyllosilicate samples [abstract 1258]. In *42nd Lunar and Planetary Science Conference*, Lunar and Planetary Institute, Houston.

Eigenbrode, J.L., Summons, R.E., Steele, A., Freissinet, C., Millan, M., Navarro-González, R., Sutter, B., McAdam, A.C., Franz, H.B., Glavin, D.P., Archer Jr., P.D., Mahaffy, P.R., Conrad, P.G., Hurowitz, J.A., Grotzinger, J.P., Gupta, S., Ming, D.W., Sumner, D.Y., Szopa, C., Malespin, C., Buch, A., and Coll, P. (2018) Organic matter preserved in 3-billion-year-old mudstones at Gale crater, Mars. *Science* 360:1096–1101.

Flynn, G.J. (1996) The delivery of organic matter from asteroids and comets to the early surface of mars. *Earth Moon Planets* 72:469–474.

Forni, O., Gaft, M., Toplis, M.J., Clegg, S.M., Maurice, S., Wiens, R.C., Mangold, N., Gasnault, O., Sautter, V., Le Mouélic, S., Meslin, P.-Y., Nachon, M., McInroy, R.E., Ollila, A.M., Cousin, A., Bridges, J.C., Lanza, N.L., and Dyar, M.D. (2015) First detection of fluorine on Mars: implications for Gale Crater's geochemistry. *Geophys Res Lett* 42:1020–1028.

Forni, O., Meslin, P.-Y., L'Haridon, J., Rapin, W., Nachon, M., Newsom, H., Mangold, N., Gasnault, O., Anderson, D.E., Anderson, R.B., Blaney, D.L., Clegg, S.M., Cousin, A., Dehouck, E., Johnson, J.R., Lanza, N.L., Lasue, J., Maurice, S., and Wiens, R.C. (2017) Detection of fluorine-rich phases, phosphates, and halite in the stimson-murray units, Gale Crater, Mars [abstract 1838]. In *48th Lunar and Planetary Science Conference*, Lunar and Planetary Institute, Houston.

Freissinet, C., Glavin, D.P., Mahaffy, P.R., Miller, K.E., Eigenbrode, J.L., Summons, R.E., Brunner, A.E., Buch, A., Szopa, C., Archer, P.D., Jr., Franz, H.B., Atreya, S.K., Brinckerhoff, W.B., Cabane, M., Coll, P., Conrad, P.G., Des Marais, D.J., Dworkin, J.P., Fairén, A.G., François, P., Grotzinger, J.P., Kashyap, S., ten Kate, I.L., Leshin, L.A.,

Malespin, C.A., Martin, M.G., Martin-Torres, F.J., McAdam, A.C., Ming, D.W., Navarro-González, R., Pavlov, A.A., Prats, B.D., Squyres, S.W., Steele, A., Stern, J.C., Sumner, D.Y., Sutter, B., and Zorzano, M.-P.; the MSL Science Team. (2015) Organic molecules in the Sheepbed Mudstone, Gale Crater, Mars. *J Geophys Res* 120:495–514.

Furrer, G. and Stumm, W. (1986) The coordination chemistry of weather: 1. dissolution kinetics of δ-Al$_2$O$_3$ and BeO. *Geochim Cosmochim Acta* 50:1847–1860.

Gainey, S.R., Hausrath, E.M., Adcock, C.T., Tschauner, O., Hurowitz, J.A., Ehlmann, B.L., Xiao, Y., and Bartlett, C.L. (2017) Clay mineral formation under oxidized conditions and implications for paleoenvironments and organic preservation on Mars. *Nat Commun* 8:1230.

Goyne, K.W., Brantley, S.L., and Chorover, J. (2006) Effects of organic acids and dissolved oxygen on apatite and chalcopyrite dissolution: implications for using elements as organomarks and oxymarkers. *Chem Geolo* 243:28–45.

Greenwood, J.P., Blake, R.E., and Coath, C.D. (2003) Ion microprobe measurements of 18O/16O ratios of phosphate minerals in the martian meteorites ALH84001 and Los Angeles. *Geochim Cosmochim Acta* 67:2289–2298.

Grotzinger, J.P., Sumner, D.Y., Kah, L.C., Stack, K., Gupta, S., Edgar, L., Rubin, D., Lewis, K., Schieber, J., Mangold, N., Milliken, R., Conrad, P.G., DesMarais, D., Farmer, J., Siebach, K., Calef, F., 3rd, Hurowitz, J., McLennan, S.M., Ming, D., Vaniman, D., Crisp, J., Vasavada, A., Edgett, K.S., Malin, M., Blake, D., Gellert, R., Mahaffy, P., Wiens, R.C., Maurice, S., Grant, J.A., Wilson, S., Anderson, R.C., Beegle, L., Arvidson, R., Hallet, B., Sletten, R.S., Rice, M., Bell, J., 3rd, Griffes, J., Ehlmann, B., Anderson, R.B., Bristow, T.F., Dietrich, W.E., Dromart, G., Eigenbrode, J., Fraeman, A., Hardgrove, C., Herkenhoff, K., Jandura, L., Kocurek, G., Lee, S., Leshin, L.A., Leveille, R., Limonadi, D., Maki, J., McCloskey, S., Meyer, M., Minitti, M., Newsom, H., Oehler, D., Okon, A., Palucis, M., Parker, T., Rowland, S., Schmidt, M., Squyres, S., Steele, A., Stolper, E., Summons, R., Treiman, A., Williams, R., and Yingst, A.; MSL Science Team. (2014) A habitable fluvio-lacustrine environment at Yellowknife Bay, Gale Crater, Mars. *Science* 343:1242777.

Guidry, M.W. and Mackenzie, F.T. (2003) Experimental study of igneous and sedimentary apatite dissolution: control of pH, distance from equilibrium, and temperature on dissolution rates. *Geochim Cosmochim Acta* 67:2949–2963.

Hausrath, E.M., Neaman, A., and Brantley, S.L. (2009) Elemental release rates from dissolving basalt and granite with and without organic ligands. *AJS* 309:633–660.

Hausrath, E.M., Navarre-Sitchler, A.K., Sak, P.B., Williams, J.Z., and Brantley, S.L. (2011) Soil profiles as indicators of mineral weathering rates and organic interactions on a Pennsylvania diabase. *Chem Geol* 290:89–100.

Hausrath, E.M., Golden, D.C., Morris, R.V., Agresti, D.G., and Ming, D.W. (2013) Acid sulfate alteration of fluorapatite, basaltic glass and olivine by hydrothermal vapors and fluids: implications for fumarolic activity and secondary phosphate phases in sulfate-rich Paso Robles soil at Gusev Crater, Mars. *J Geophys Res* 118:1–13.

Hayes, J.M. and Biemann, K. (1968) High resolution mass spectrometric investigations of the organic constituents of the Murray and Holbrook chondrites. *Geochim Cosmochim Acta* 32:239–267.

Hays, L.R., Graham, H.V., Des Marais, D.J., Hausrath, E.M., Horgany, B., McCollom, T.M., Parenteau, M.N., Potter-McIntyre, S.L., Williams, A.J., and Lynch, K.L. (2017) Biosignature preservation and detection in Mars analog environments. *Astrobiology* 17:4.

Hewins, R., Zanda, B., Humayun, M., Pont, S., Fieni, C., and Deldicque, D. (2013) Northwest Africa 7533, an impact breccia from Mars. *LPI Contributions* 1719:2385.

Heyer, H. and Krumbein, W.E. (1991) Excretion of fermentation products in dark and anaerobically incubated cyanobacteria. *Arch Microbiol* 155:284–287.

Huang, Y., Wang, Y., Alexandre, M., Lee, T., Rose-Petruck, C., Fuller, M., and Pizzarello, S.. (2005) Molecular and compound-specific isotopic characterization of monocarboxylic acids in carbonaceous meteorites. *Geochim Cosmochim Acta* 69:1073–1084.

Hughes, J.M., Jolliff, B.I., and Rakovan, J. (2008) The crystal chemistry of whitlockite and merrillite and the dehydrogenation of whitlockite to merrillite. *Am Mineral* 93:1300–1305.

Hurowitz, J.A., McLennan, S.M., McSween, H.Y., DeSouza, P.A.J., and Klingelhofer, G. (2006) Mixing relationships and the effects of secondary alteration in the Wishstone and Watchtower Classes of Husband Hill, Gusev Crater, Mars. *J Geophys Res* 111. e12514; doi: 10.1029/2006JE002795

Jenneman, G.E., McInerney, M.J., Crocker, M.E., and Knapp, R.M. (1986) Effect of sterilization by dry heat or autoclaving on bacterial penetration through Berea sandstone. *Appl Environ Microbiol* 51:39–43.

Kounaves, S.P., Hecht, M.H., Kapit, J., Quinn, R.C., Catling, D.C., Clark, B.C., Ming, D.W., Gospodinova, K., Hredzak, P., McElhoney, K., and Shusterman, J. (2010) Soluble sulfate in the martian soil at the Phoenix landing site. *Geophys Res Lett* 37. L09201; doi: 10.1029/20104042613.

Lane, M.D., Bishop, J.L., Darby Dyar, M., King, P.L., Parente, M., and Hyde, B.C. (2008) Mineralogy of the Paso Robles soils on Mars. *Am Mineral* 93:728–739.

Madigan, M.T., Martinko, J.M., and Parker, J. (2003) *Brock Biology of Microorganisms*, Pearson Education, Upper Saddle River, NJ, p 1385.

Martell, A.E. and Smith, R.M. (1974) *Critical stability Constants*, Plenum Press, New York, p 1.

Maurice, S., Wiens, R.C., Saccoccio, M., Barraclough, B., Gasnault, O., Forni, O., Mangold, N., Baratoux, D., Bender, S., Berger, G., Bernardin, J., Berthé, M., Bridges, N., Blaney, D., Bouyé, M., Cais, P., Clark, B., Clegg, S., Cousin, A., Cremers, D., Cros, A., DeFlores, L., Derycke, C., Dingler, B., Dromart, G., Dubois, B., Dupieux, M., Durand, E., d'Uston, L., Fabre, C., Faure, B., Gaboriaud, A., Gharsa, T., Herkenhoff, K., Kan, E., Kirkland, L., Kouach, D., Lacour, J.-L., Langevin, Y., Lasue, J., Le Mouélic, S., Lescure, M., Lewin, E., Limonadi, D., Manhes, G., Mauchien, P., McKay, C., Meslin, P.-Y., Michel, Y., Miller, E., Newsom, H.E., Orttner, G., Paillet, A., Pares, L., Parot, Y., Perez, R., Pinet, P., Poitrasson, F., Quertier, B., Sallé, B, Sotin, C., Sautter, V., Seran, H., Simmonds, J.J., Sirven, J.-B., Stiglich, R., Streibig, N., Thocaven, J.-J., Toplis, M., and Vaniman, D. (2012) The ChemCam instruments on the Mars Science Laboratory (MSL) rover: science objectives and mast unit. *Space Sci Rev* 170:95–166.

McClellan, G. and Van Kauwenbergh, S. (1990) *Mineralogy of Sedimentary Apatites*, Special Publications, Vol. 52, Geological Society, London, pp 23–31.

McCubbin, F.M. and Nekvasil, H. (2008) Maskelynite-hosted apatite in the Chassigny meteorite: insights into late-stage magmatic volatile evolution in martian magmas. *Am Mineral* 93:9.

McCubbin, F.M., Boyce, J.W., Srinivasan, P., Santos, A.R., Elardo, S.M., Filiberto, J., Steele, A., and Shearer, C.K. (2016) Heterogeneous distribution of H$_2$O in the martian

interior: implications for the abundance of H$_2$O in depleted and enriched mantle sources. *Meteorit Planet Sci* 51:2036–2060.

McKelvey, V. (1973) Abundance and distribution of phosphorus in the lithosphere. In *Environmental Phosphorus Handbook*, edited by E.J. Griffith, A. Beeton, J.M. Spencer, and D.T. Mitchell, Wiley, New york. pp 13–31.

McSween, H. and Treiman, A.H. (1998) Martian meteorites. In *Planetary Materials*, edited by J. Papike, Mineral Society of America, Washington, DC. pp 6:01–6:53.

Meslin, P.-Y., Cicutto, L., Forni, O., Drouet, C., Rapin, W., Nachon, M., Cousin, A., Blank, J.G., McCubbin, F.M., and Gasnault, O. (2016) Calibration of the fluorine, chlorine and hydrogen content of apatites with the ChemCam LIBS instrument [abstract 1703]. In *Lunar and Planetary Science Conference*, Lunar Planetary Institute, Houston.

Miller, K.E., Eigenbrode, J.L., Freissinet, C., Glavin, D.P., Kotrc, B., Francois, P., and Summons, R.E. (2016) Potential precursor compounds for chlorohydrocarbons detected in Gale Crater, Mars, the SAM instrument suite on the curiosity rover. *J Geophys Res* 121:296–308.

Ming, D.W., Gellert, R., Morris, R.V., Arvidson, R.E., Brückner, J., Clark, B.C., Cohen, B.A., d'Uston, C., Economou, T., Fleischer, I., Klingelhöfer, G., McCoy, T.J., Mittlefehldt, D.W., Schmidt, M.E., Schröder, C., Squyres, S.W., Tréguier, E., Yen, A.S., and Zipfel, J. (2008) Geochemical properties of rocks and soils in Gusev Crater, Mars: results of the alpha particle X-ray spectrometer from Cumberland Ridge to home plate. *J Geophys Res* 113:S39.

Murphy, J. and Riley, J.P. (1962) A modified single solution method for the determination of phosphate in natural waters. *Anal Chim Acta* 27:31–36.

Neaman, A., Chorover, J., and Brantley, S. (2005) Implications of the evolution of organic acid moieties for basalt weathering over geologic time. *AJS* 305:625–650.

Olsen, A.A. and Rimstidt, J.D. (2008) Oxalate-promoted forsterite dissolution at low pH. *Geochim Cosmochim Acta* 72:1758–1766.

Parkhurst, D.L. and Appelo, C.A.J. (1999) User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculation. *US Geol Survey Water-Resources Invest Rept* 99–4259.

Pasek, M. and Block, K. (2009) Lightning-induced reduction of phosphorus oxidation state. *Nat Geosci* 2:553–556.

Pasek, M. and Kee, T. (2011) On the origin of phosphorylated biomolecules. In *Origins of Life: The Primal Self-Organization*, edited by R. Egel, D.-H. Lankenau, and A.Y. Mulkidjanian, Springer, Berlin Heidelberg. pp 57–84.

Pizzarello, S. and Huang, Y. (2002) Molecular and isotopic analyses of Tagish Lake alkyl dicarboxylic acids. *Meteorit Planet Sci* 37:687–696.

Pizzarello, S., Cooper, G.W., and Flynn, G.J. (2006) The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles. In *Meteorites and the Early Solar System II*, edited by D.S. Lauretta and H.Y. McSween, Jr. University of Arizona Press, Tucson. pp 625–651.

Powner, M.W., Gerland, B., and Sutherland, J.D. (2009) Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions. *Nature* 459: 239–242.

Prener, J.S. (1967) The growth and crystallographic properties of calcium-fluor and chlorapatite minerals. *J Electrochem Soc* 114:77–83.

Prener, J.S. (1971) Nonstoichiometry in calcium chlorapatite. *J Solid State Chem* 3:49–55.

Prescott, L.M., Harley, J.P., and Klein, D.A. (1996) *Microbiology*, William C. Brown Publishers, Dubuque, IA, p 935.

Quirico, E., Orthous-Daunay, F.-R., Beck, P., Bonal, L., Brunetto, R., Dartois, E., Pino, T., Montagnac, G., Rouzaud, J.-N., Engrand, C., and Duprat, J. (2014) Origin of insoluble organic matter in type 1 and 2 chondrites: new clues, new questions. *Geochim Cosmochim Acta* 136(Suppl C):80–99.

Rampe, E.B., Ming, D.W., Blake, D.F., Bristow, T.F., Chipera, S.J., Grotzinger, J.P., Morris, R.V., Morrison, S.M., Vaniman, D.T., Yen, A.S., Achilles, C.N., Craig, P.I., Des Marais, D.J., Downs, R.T., Farmer, J.D., Fendrich, K.V., Gellert, R., Hazen, R.M., Kah, L.C., Morookian, J.M., Peretyazhko, T.S., Sarrazin, P., Treiman, A.H., Berger, J.A., Eigenbrode, J., Fairén, A.G., Forni, O., Gupta, S., Hurowitz, J.A., Lanza, N.L., Schmidt, M.E., Siebach, K., Sutter, B., and Thompson, L.M. (2017). Mineralogy of an ancient lacustrine mudstone succession from the Murray formation, Gale crater, Mars. *Earth Planet Sci Lett* 471:172–185.

Santos, A.R., Agee, C.B., McCubbin, F.M., Shearer, C.K., Burger, P.V., Tartèse, R., and Anand, M. (2015) Petrology of igneous clasts in Northwest Africa 7034: implications for the petrologic diversity of the martian crust. *Geochim Cosmochim Acta* 157:56–85.

Shearer, C.K., Burger, P.V., Papike, J.J., Sharp, Z.D., and McKeegan, K.D. (2011) Fluids on differentiated asteroids: evidence from phosphates in differentiated meteorites GRA 06128 and GRA 06129. *Meteorit Planet Sci* 46:1345–1362.

Shearer, C., Burger, P., Papike, J., McCubbin, F., and Bell, A. (2015) Crystal chemistry of merrillite from martian meteorites: mineralogical recorders of magmatic processes and planetary differentiation. *Meteorit Planet Sci* 50:649–673.

Stumm, W. (1997) Reactivity at the mineral-water interface: dissolution and inhibition. *Colloids Surf A Physicochem Eng Asp* 120:143–166.

Tacker, R.C. and Stormer, J.C., Jr. (1993) Thermodynamics of mixing of liquids in the system Ca$_3$(PO$_4$)$_2$-CaCl$_2$-CaF$_2$-Ca(OH)$_2$. *Geochim Cosmochim Acta* 57:4663–4676.

Tan, K.H. (1986) Degradation of soil minerals by organic acids. In *Interactions of Soil Minerals with Natural Organics and Microbes*, edited by P.M. Huang and M. Schnitzer, Soil Science Society of America, Madison, WI, pp 1–27.

Tanaka, H., Miyajima, K., Nakagaki, M., and Shimabayahi, S. (1989) Interactions of aspartic acid, alanine and lysine with hydroxyapatite. *Chem Pharm Bull* 37:2897–2901.

Thompson, A.S., Owens, N.J.P., and Murrell, J.C. (1995) Isolation and characterization of methanesulfonic acid-degrading bacteria from the marine environment. *Appl Environ Microbiol* 61:2388–2393.

Treiman, A.H., Bish, D.L., Vaniman, D.T., Chipera, S.J., Blake, D.F., Ming, D.W., Morris, R.V., Bristow, T.F., Morrison, S.M., and Baker, M.B. (2016) Mineralogy, provenance, and diagenesis of a potassic basaltic sandstone on Mars: CheMin X-ray diffraction of the Windjana sample (Kimberley area, Gale Crater). *J Geophys Res Planets* 121:75–106.

Tucker, J.M., Dyar, M.D., Schaefer, M.W., Clegg, S.M., and Wiens, R.C. (2010) Optimization of laser-induced breakdown spectroscopy for rapid geochemical analysis. *Chem Geol* 277: 137–148.

Udry, A., Lunning, N.G., McSween, H.Y., and Bodnar, R.J. (2014) Petrogenesis of a vitrophyre in the martian meteorite breccia NWA 7034. *Geochim Cosmochim Acta* 141:281–293.

Valsami-Jones, E., Ragnarsdottir, K.V., Putnis, A., Bosbach, D., Kemp, A.J., and Cressey, G. (1998) The dissolution of apatite in the presence of aqueous metal cations at pH 2–7. *Chem Geol* 151:215–233.

Welch, S.A. and Ullman, W.J. (2000) The temperature dependence of bytownite feldspar dissolution in neutral aqueous solutions of inorganic and organic ligands at low temperature (5–35°C). *Chem Geol* 167:337–354.

Welch, S.A., Taunton, A.E., and Banfield, J.F. (2002) Effect of microorganisms and microbial metabolites on apatite dissolution. *Geomicrobiol J* 19:343–367.

White, A.F. and Brantley, S.L. (2003) The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chem Geol* 202:479–506.

Wiens, R.C., Maurice, S., Barraclough, B., Saccoccio, M., Barkley, W.C, Bell, J.F., III, Bender, S., Bernardin, J., Blaney, D., Blank, J., Bouye, M., Bridges, N., Cais, P., Clanton, R.C., Clark, B., Clegg, S., Cousin, A., Cremers, D., Cros, A., De-Flores, L., Delapp, D., Dingler, R., D'Uston, C., Dyar, M.D., Elliott, T., Enemark, D., Fabre, C., Flores, M., Forni, O., Gasnault, O., Hale, T., Hays, C., Herkenhoff, K., Kan, E., Kirkland, L, Kouach, D., Landis, D., Langevin, Y., Lanza, N., LaRocca, F., Lasue, J., Latino, J., Limonadi, D., Lindensmith, C., Little, C., Mangold, N., Manhes, G., Mauchien, P., McKay, C., Miller, E., Mooney, J., Morris, R.V., Morrison, L., Nelson, T., Newsom, H., Ollila, A., Ott, M., Pares, L., Perez, R., Poitrasson, F., Provost, C., Reiter, J.W., Roberts, T., Romero, F., Sautter, V., Salazar, S., Simmonds, J.J., Stiglich, R., Storms, S., Streibig, N., Thocaven, J.-J., Trujillo, T., Ulibarri, M., Vaniman, D., Warner, N., Waterbury, R., Whitaker, R., Witt, J., and Wong-Swanson, B. (2012) The ChemCam instruments on the Mars Science Laboratory (MSL) rover: body unit and combined system performance. *Space Sci Rev* 170:167–227.

Willis, J.B. (1962) Determination of lead and other heavy metals in urine by atomic absorption spectrophotometry. *Anal Chem* 34.

Wu, L.P., Munakata, M., Kuroda-Sowa, T., Maekawa, M., and Suenaga, Y. (1996) Synthesis, crystal structures and magnetic behavior of polymeric lanthanide complexes with benzene-hexacarboxylic acid (mellitic acid). *Inorg Chim Acta* 249: 183–189.

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Abbreviations Used	
AA	= atomic absorption
DCPA	= di-calcium phosphate anhydrous
ICP-MS	= inductively coupled plasma mass spectrometer
IDPs	= interplanetary dust particles
LIBS	= laser-induced breakdown spectroscopy
SAM	= Sample Analysis at Mars
SI	= saturation index
SOM	= supplementary online materials