

PHOSPHATE RELEASE: THE EFFECT OF PREBIOTIC ORGANIC COMPOUNDS ON DISSOLUTION OF MARS-RELEVANT PHOSPHATE MINERALS. C. L. Bartlett¹, E. M. Hausrath¹, and C. T. Adcock¹, ¹Department of Geoscience, University of Nevada, Las Vegas, NV 89154, bartlc1@unlv.nevada.edu

Introduction: Phosphate is essential for life; it is required to stabilize RNA, DNA as well as phospholipid membranes [1]. Phosphorus, either as phosphate or a more reduced form such as phosphite, may also have played an important role in prebiotic reactions [2-3]. The dominant phosphate-bearing minerals found in Martian meteorites are merrillite, $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$, and chlorapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{Cl}, \text{F})$. When phosphate-containing minerals dissolve, the phosphate contained within the mineral becomes available for use by organisms, or prebiotic reactions. Therefore, the study of how minerals release phosphate is essential for not only determining how much phosphate could be available, but what influences its release. To the best of our knowledge, no studies have examined the effect of organic compounds on either merrillite or chlorapatite dissolution. This study aims to further the knowledge of phosphate availability from mineral surfaces through dissolution experiments of Mars-relevant phosphate-bearing minerals in the presence of prebiotic organic compounds, with implications for habitability on Mars.

Phosphate availability is a crucial factor in determining whether Mars was once habitable. Previous work has suggested that phosphate availability on early Mars may have been greater than phosphate availability on early Earth based on dissolution experiments of merrillite and chlorapatite in abiotic, inorganic solutions [4]. However, the environments in which phosphate release would have been most relevant to potential early martian life likely did not contain solely inorganic solutions and phosphate mineral surfaces, but also likely contained abundant organic matter delivered by carbonaceous chondrites and interplanetary dust particles [5].

The organic material found in carbonaceous chondrites encompasses a broad range of compounds, including alkyl amino acids, cycloalkane amino acids, alkanedioic acids, dicarboxylic acids, and carboxylic acids (the most concentrated soluble organic compounds in carbonaceous chondrites) [6-8]. The presence of these organic compounds may have played an important role in the reactions leading to life on Earth and/or Mars. These organic compounds may also have played an important role in phosphate mobility in early, potentially habitable, martian environments. Studies have shown that the presence of organic compounds can enhance phosphate release in hydroxyapatite by complexing calcium [9-11]. Based on previous

measurements, a series of seven prebiotic organic compounds was chosen: aspartic acid, acetate, propanate, succinic acid, glutaric acid, oxalic acid, and methylsulfonic acid.

Methods: Merrillite was synthesized by the deprotonation of whitlockite following Hughes et al. [12]. Chlorapatite was synthesized by methods similar to Adcock et al. [4]. A weight ratio of 6:7.5 hydroxyapatite to calcium chloride was heated to 1100 degrees Celsius for 24 hours. Chlorapatite and merrillite were confirmed using X-ray diffraction (XRD) and electron microprobe (EMP). Before beginning the dissolution experiments, merrillite and chlorapatite were powdered by mortar and pestle, sieved to the 75-150 μm size fraction, and washed until no fine particles were observed on mineral surfaces by Scanning Electron Microscopy (SEM). The sodium salt of each organic compound chosen was used for experimentation.

For each dissolution experiment 0.1500 g of merrillite or chlorapatite was placed in 180 mL of solution in 250 mL low density polyethylene (LDPE) bottles. Each organic acid solution, containing 0.05 M of the organic compound used, was then adjusted to a pH of 5.5. The pH was chosen based on the pK values of the acids used as well as a common pH for natural solutions on Earth and possibly also on Mars. Each condition was run in duplicate, with organic-free controls for each mineral also conducted in duplicate. At least one blank was also run for each condition. Batches were sampled at predetermined time intervals. For each sampling period, 10 mL of solution was removed via pipet and tested for pH as well as calcium and phosphate concentrations. The presence of calcium in solution was measured using atomic absorption (AA) spectrometry on a Thermo Scientific iCE 3000 Series AA after adding 0.36 M lanthanum chloride solution to 10% v/v to mitigate interference by phosphorus. Phosphorus was measured by the methyl blue / acetic acid method using a Thermo Scientific Genesys 10S UV-Vis.

Results: Results of this study will provide further understanding of the dissolution of the dominant Mars-relevant phosphate-containing minerals chlorapatite and merrillite in the presence of organic compounds. This has important implications for the possible habitability of Mars. Understanding phosphate mobility in the presence of prebiotic organic compounds will help better interpret the potential habitability of early martian environments.

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