

**FE-PHOSPHATES IN THE JEZERO CRATER FAN: IMPLICATIONS FOR HABITABILITY AND SAMPLE RETURN.** T.V. Kizovski<sup>1</sup>, M.E. Schmidt<sup>1</sup>, L. O'Neil<sup>2</sup>, D. Klevang<sup>3</sup>, N. Tosca<sup>4</sup>, M. Tice<sup>2</sup>, M. Cable<sup>5</sup>, E. Hausrath<sup>6</sup>, C.T. Adcock<sup>6</sup>, J. Hurowitz<sup>7</sup>, A. Treiman<sup>8</sup>, M. Jones<sup>9</sup>, F.M. McCubbin<sup>10</sup>, A. Allwood<sup>5</sup>, Y. Liu<sup>5</sup>, S. Sharma<sup>5</sup>, B. Clark<sup>11</sup>, S. VanBommel<sup>12</sup>, J. Christian<sup>12</sup>, A. Knight<sup>12</sup>, J. Labrie<sup>1</sup>, P. Lawson<sup>5</sup>, D. Catling<sup>13</sup>, E. Cloutis<sup>14</sup>, L. Wade<sup>5</sup>, C. Heirweh<sup>5</sup>, T. Elam<sup>13</sup>, N. Randazzo<sup>15</sup>, C.D.K Herd<sup>15</sup>. <sup>1</sup>Brock U. (St. Catharines, ON, L2S 3A1, Canada, [kizovski@brocku.ca](mailto:kizovski@brocku.ca)), <sup>2</sup>Texas A&M (College Station, TX), <sup>3</sup>DTU Space (Kongens Lyngby, Denmark), <sup>4</sup>Cambridge U. (Cambridge, UK), <sup>5</sup>JPL-Caltech (Pasadena, CA), <sup>6</sup>UNLV (Las Vegas, NV), <sup>7</sup>NY Stony Brook (NY), <sup>8</sup>LPI/USRA (Houston, TX), <sup>9</sup>QUT (Brisbane, Australia), <sup>10</sup>NASA JSC (Houston, TX), <sup>11</sup>Space Sci. Inst. (Boulder, CO), <sup>12</sup>Wash.U (St. Louis, MO), <sup>13</sup>U. Wash. (Seattle, WA), <sup>14</sup>U. Winn. (Winnipeg, Canada), <sup>15</sup>U. Alberta (Edmonton, Canada)

**Introduction:** In the ~1000 sols since the Mars 2020 *Perseverance* rover landed on the floor of Jezero crater, it has traversed >23 km, carrying out analyses of the crater floor and western fan. The fan is comprised of sediments transported and deposited by streams that once flowed into Jezero crater in the late Noachian to early Hesperian [1]. Detailed investigation of the sediments and rocks of the western fan can thus provide insights into ancient fluvial to lacustrine environments on Mars, whether they were habitable, and/or if biosignatures may be preserved.

Here, we report the mineralogical and chemical analyses of a conglomerate outcrop (informally named Onahu) on top of the western fan. This outcrop is of particular interest as it contains large (~100s  $\mu\text{m}$ ) blue-green Fe-phosphate minerals (Fig. 1). Fe-phosphates are rare on Earth and Mars, which are both dominated by Ca-phosphates. Phosphate minerals are high value targets for Mars sample return because their chemistry and textural occurrence can be used to constrain the bioavailability of P for prebiotic chemical reactions and/or potential life, past aqueous conditions on Mars (i.e., pH, T, etc.); and when igneous in origin, insights into magmatic volatile abundances. Fe-phosphate minerals are particularly important astrobiological targets as they have been observed in several localities on Earth encrusting bacterial cells (i.e., [2]) and growing on organic matter including bones, fossils, shells, and teeth [3].

Due to the rarity of Fe-phosphates on Mars, and the wealth of paleoenvironmental and astrobiological information that can be obtained through their detailed study, this work summarizes the chemical, reflectance, and micro-structural analysis of the Onahu Fe-phosphates carried out by the Planetary Instrument for X-ray Lithochemistry (PIXL).

**Methods:** High-resolution X-ray fluorescence (XRF) mapping by PIXL was carried out on a 50 mm circular abrasion patch (dubbed Ouzel Falls), on the pebbly conglomerate outcrop Onahu. PIXL obtained three XRF raster scans on Sols 789, 790, and 811, with a total scan area of 97 mm<sup>2</sup> and step sizes of 0.125 mm. PIXL's Micro Context Camera (MCC) also acquired reflectance images illuminated by ultraviolet (UV, 385 nm), blue (B, 450 nm), green (G, 530 nm) and near-infrared (NIR, 735 nm) light emitting diodes. A sample core (Otis

Peak) was collected from the same stratigraphic and lithological unit as Onahu on Sol 882



**Figure 1:** WATSON images and PIXL XRF maps showing the location of the blue-green Fe-phosphate minerals in Ouzel Falls. Approximate footprints of the PIXL scans are shown in A & B.

**Results:** Ouzel Falls is predominantly comprised of gravel- to pebble-sized clasts of olivine, altered mafic material, and carbonates embedded in a fine-grained matrix. The matrix includes domains rich in Si and domains rich in carbonate, intermixed with fine-grained fragments of the major clast types.

Fe-phosphates were identified in the carbonate-bearing matrix domain. The phosphates are recognized by high concentrations of P and Fe in the PIXL maps, which correlate with ~50-500  $\mu\text{m}$  green-blue grains in WATSON images (Fig. 1). Due to their small size, no PIXL points were collected in pure Fe-phosphate. All of the measured XRF compositions are instead mixtures of Fe-phosphate and surrounding matrix (with elevated Si, S, etc. compared to pure Fe-phosphate). Thus, the Fe-phosphate composition is determined here using mixing trends with matrix minerals (projecting compositional mixing lines between other Onahu phases and the high Fe-P points down to 0% SiO<sub>2</sub>; Fig. 2). These mixing trends indicate the Fe-phosphates have Fe:P molar ratios of ~3:2. There is also no strong correlation between Ca and P, indicating that Ca-phosphates are not major components in Ouzel Falls, although they are common in Jezero crater [4,5].

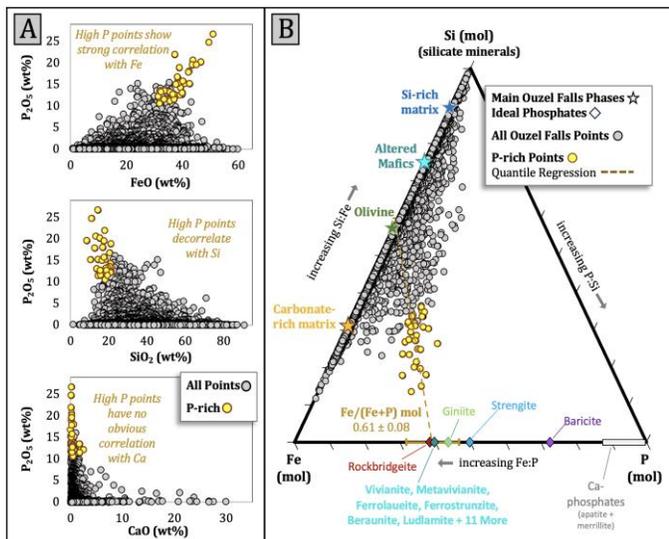


Figure 2: (A) PIXL XRF data showing how high P points are correlated with high Fe and decorelated with Si and Ca. (B) Ternary diagram illustrating mixing between Ouzel Falls silicates, carbonates, and Fe-phosphates.

X-ray diffraction peaks are also detected by PIXL in the P-rich regions, indicating that the Fe-phosphates are crystalline. Reflectance spectra from PIXL’s MCC show that the Fe-phosphates have high G/NIR signatures compared to the rest of the patch, but still have significant NIR reflectance. This may be due to mixing between the blue-green phosphates and surrounding phases at the MCC images’ resolution.

#### Discussion: Fe-Phosphate Phase Determination:

A wide variety of Fe-phosphate minerals have Fe:P ratios similar to those in Ouzel Falls (Fe/P ~3/2; Fe/(Fe+P) mol = 0.61 ± 0.08; Fig. 2). According to the International Mineralogical Association RRUFF database [6], 23 known Fe-phosphate minerals have Fe:P ratios similar to those in Onahu. These minerals can be differentiated based on crystal structure, color, Fe-oxidation, and H<sub>2</sub>O content.

X-ray diffraction patterns from PIXL data can be used for high-level crystal structure determination [7], and in the high-P regions appear most consistent with that of metavivianite (Fe<sup>2+</sup>Fe<sup>3+</sup><sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>•6H<sub>2</sub>O). Meta-vivianite is a secondary phase, that forms by oxidation of the Fe-phosphate mineral vivianite (Fe<sup>2+</sup><sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>•8(H<sub>2</sub>O)). Vivianite is the most common Fe-phosphate on Earth, and is found in a variety of igneous, sedimentary, and biologic environments [3].

One of vivianite’s distinguishing properties is its blue-green color that occurs due to Fe-oxidation when exposed to air [8]. Meta-vivianite (triclinic) forms from vivianite (monoclinic) as Fe<sup>3+</sup> increases, resulting in a degradation of crystal symmetry [8]. The blue-green color of the Onahu Fe-phosphates is similar to terrestrial vivianites, however many of the 23 Fe-phosphates considered here can also occur in blue/green colors.

While PIXL is unable to directly measure Fe<sup>3+</sup> or H, concentrations of H<sub>2</sub>O (and other low Z elements) can be indirectly estimated by PIXL when low analytical

totals are reported. As a first order estimate of H<sub>2</sub>O content in the Fe-phosphates, the most abundant mixing phase (olivine) was stoichiometrically stripped from the raw XRF composition of the highest-P PIXL points. The resulting “stripped” composition indicates the Fe-phosphates contain ~30 wt% H<sub>2</sub>O (assuming all of the unmeasured component is water). Based on this, the Fe-phosphates are again very similar to vivianite (i.e., stoichiometric vivianite has ~28.7 wt% H<sub>2</sub>O).

#### Paleoenvironmental Conditions

As Fe-phosphates can occur in a variety of environments on Earth, narrowing down the conditions that led to their formation on Mars is equivocal. At a high-level, the presence of Fe-phosphates in Onahu and lack of Ca-phosphates indicates that the magma or fluid that they crystallized from was Ca-poor [9].

It is not obvious at this time if the Fe-phosphates at Onahu are detrital or formed in place. If detrital, they could have originally crystallized as primary igneous phases from a highly evolved magmato-hydrothermal system (like a granite pegmatite), or formed during weathering of a Ca-phosphate bearing ultramafic rock [10]. However, on Earth Fe-phosphates like vivianite are more commonly found as precipitates in freshwater or marine sediments, occurring in close association with organics, and as biogenic minerals produced by metal reducing bacteria [3]. In terrestrial aqueous environments, vivianite forms in anoxic, reducing, S-poor conditions at ~neutral pH, where there are high concentrations of dissolved Fe<sup>2+</sup> and P [3,11]. These conditions can occur as a result of microbial degradation of organic matter and reductive Fe-oxide/hydroxide dissolution [11], but organics and microbial activity are not essential for vivianite formation. For example, on Mars, vivianite alteration products have been observed in Mn-P-rich nodules in Gale Crater [12]. The vivianite in that case likely precipitated from a locally P- and Mn-rich reduced groundwater, filling sediment pore spaces [12].

#### Implications for Mars Sample Return

Further work is underway to constrain exactly which Fe-phosphate phase(s) are in the Onahu conglomerate, and the conditions under which they formed. While the Perseverance rover’s instrument payload can provide immense amounts of information on exciting minerals like the Fe-phosphates described here, detailed analysis of the corresponding Otis Peak sample on Earth will be essential to confirm their igneous, aqueous, or even possible biologic origin.

**References:** [1] Farley et al. (2022) *Science*. [2] Konhauser et al., (1994) *Can. Earth Sci.* [3] Rothe et al. (2016) *Earth Sci. Rev.* [4] Kizovski et al. (2022) *LPSC 53* abs#2384. [5] Kizovski et al. (2023) *LPSC 54* abs#2855. [6] <http://rruff.info/ima/> [7] Jones et al. (2023) *LPSC 54* abs#3006. [8] Zdenka et al., (2015) *Spectrochim Acta*. [9] Brady et al. (2022) *Nat. Comms*. [10] Hurowitz et al. (2024) *LPSC 55*. [11] Metz et al., (2023) *Environ. Sci. Technol.* [12] Treiman et al. (2023) *Mineral* 1122.