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Geochemical and Metabolomic study of few Yellowstone spring systems over a range of pH

D. Boulesteix^{1,*}, A. Buch¹, A.J. Williams², C. Szopa³, V. Abrahamsson⁴, B.L. Henderson⁴, L.L. Kivrak²,
B.L. Teece⁴, T.L. Hamilton⁵ & J.R. Havig⁵

¹ Laboratoire Génie des Procédés et Matériaux, CentraleSupélec, University Paris-Saclay, 8-10 rue Joliot-Curie, 91190, Gif-sur-Yvette, France

² Department of Geological Sciences, University of Florida, Gainesville, FL 32611, USA

³ LATMOS/IPSL, UVSQ University Paris-Saclay, Sorbonne University, CNRS, 11 Bd d'Alembert, 78280, Guyancourt, France

⁴ Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States

⁵ Department of Plant and Microbial Biology, University of Minnesota Twin Cities, Saint Paul, MN 55108, USA

* Corresponding author: E-mail address: david.boulesteix@hotmail.com (David Boulesteix)

Yellowstone National Park (WY, USA) contains silica-saturated hot springs [1] with chemistry driven by subsurface processes: either minimum subsurface boiling hot springs fed by the deep hydrothermal source, or hot springs in regions where extensive subsurface boiling feeding springs that are predominantly residual liquid phase, predominantly condensed vapor phase, or a mixture of the two [2]. These processes determine the geochemistry of the surface evaporates/precipitates collected for this study: i) minimum phase separation hot springs represented by alkaline (pH 8.7) at ‘Similar Geyser’ hot spring, named W1L (or SG Digitate), ii) subsurface boiling residual liquid phase enriched in chloride and sulfate represented by pH 5.1 Dante’s Inferno L1L (or DI Active), and iii) subsurface boiling vapor phase rich in hydrogen sulfide (oxidizing to sulfuric acid) represented by pH 2.4 at ‘Goldilocks’ I1L (or GI Digitate).

Each of these spring systems presented different water temperatures (25 – 80 °C) and elemental composition (*e.g.*, Si, O, C, S, Al, Na, Fe, Ca, K, Mg, As, P, and N). These geochemical parameters impact the microbial community composition. The overall mineralogy remains similar between precipitated analyzed samples with more than 90% being composed of an amorphous silica phase (Opal A). Within the remaining 10% we identified by XRD, SEM-EDS, and Raman analysis: crystalline silica forms (quartz for all and cristobalite for I1L), elemental sulfur, phosphorus, and iron. Crystalline pyrite was also present in the majority of each sample, but no sulfates or chlorine-bearing salts) [3].

pH is driven by the subsurface processes and water composition and drives microbial community composition, but does not seem to drive the mineral-organic, (a)gnostic (bio)signatures, or the sheltering of the organic matter (OM) content over time.

Metabolomic studies were conducted using different extraction protocols and analytical instruments [4,5], and revealed a wider diversity of OM and distinct biomarkers from modern systems compared to few thousand to hundred-thousand-year spring systems (10% of OM left in the ancient system compared to the modern). We detected more than 162 organic compounds, 122 were successfully identified with a flight-like pyrolysis-gas chromatograph coupled with a commercial mass spectrometer. Liquid extraction with water or MeOH/DCM and SPME enabled identification of 30 volatile analytes, including ketones, aldehydes, and carboxylic acids. Instrumentation under development (SCHAN and Orbitrap) for future spaceflight missions were used to detect additional bioindicators or biosignatures and enhance our metabolomic microbial community profiling reconstruction and microbial identification.

These biogeochemical and metabolomic studies allowed us to target and identify bioindicators and biosignatures relevant for Mars using these analog samples to describe what

OM we could observe if life appeared on Mars (similarly to [6,7]). Critically, identifying organic compounds associated with *in situ* microbial communities that can be preserved through early diagenesis are needed given potential for alteration of organic carbon material [8]. Through MSL and Mars 2020 missions, we will likely analyze ancient hydrothermal systems similar to Yellowstone and perhaps with similar Early-Earth and Early-Mars chemistry [9,10]. Regardless of whether life emerged or evolved differently on Mars, the microscopic (coupled to geochemical/elementary/isotopic analysis presented in Figure 1) and mass spectroscopy analysis from agnostic biosignatures in our Yellowstone samples may be relevant to samples from Perseverance that are being returned to Earth through the Mars Sample Return mission. Despite the absence of microscopic imaging data from Mars landers and rovers, Fig. 1 shows that a rich abundance of sulfur and/or phosphate and/or iron combined with bioindicators' or biosignatures' detection might ensure the robustness of potential past trace of life on Mars, and better inform sample selection for analysis and return moving forward.

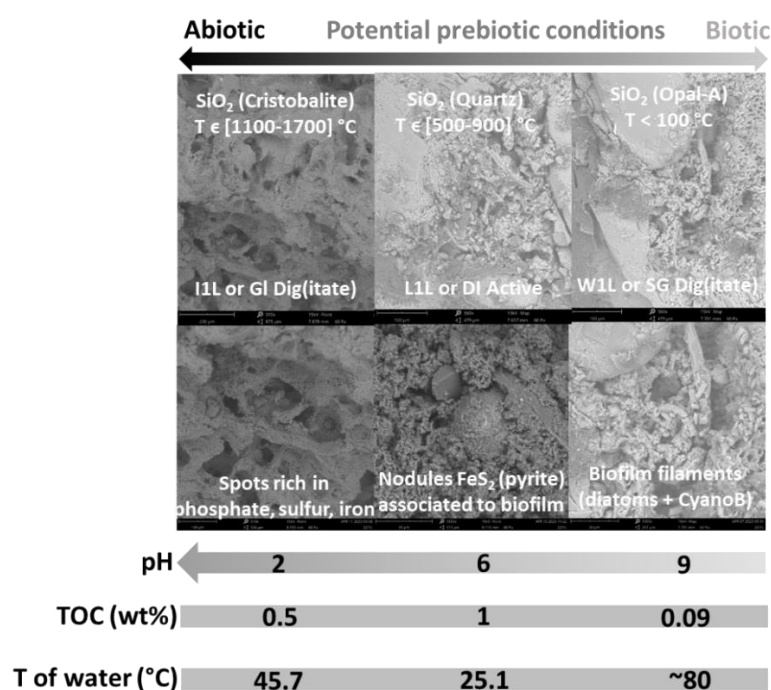


Figure 1. Agnostic signatures observed in these samples by Scanning electron microscope (SEM) and locally analyzed by energy dispersive X-ray spectroscopy (EDS) and completed with external isotopic and elementary analysis in isotope ratio mass spectrometry (IRMS).

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