FINDING ASTROBIOLOGICAL TARGETS AND POTENTIAL BIOSIGNATURES ON MARS: INSIGHTS

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Introduction: Sinters are sedimentary deposits primarily composed of opaline silica (SiO₂ $\cdot nH_2O$) and entrained detrital material [1]. They have been regarded as astrobiological targets for searching biosignatures on Mars because of their capability of preserving morphological, textural, and geochemical evidence of microbial activity [2]. Hydrated silica has been widely mapped on the surface of Mars [3], with one site at Nili Patera in Syrtis Major apparently of hydrothermal origin based solely on remote sensing data [4]. The Spirit Rover also found nearly pure hydrated silica in Gusev Crater on Mars, which is morphologically and spectrally comparable to modern silica sinters at El Tatio in Chile [5], making it one of the most appealing targets for astrobiological exploration [6]. However, the in situ identification of carbonaceous matter in these hydrothermal silica deposits is lacking. In this study, we conducted both compositional remote sensing and laboratory measurements to aid determination of astrobiological targets and identification of potential biosignatures on Mars.

Datasets, Samples, and Methods: Compositional remote sensing was based on ASTER (15–30 m/pixel) and WorldView (1.6–3.7 m/pixel) data from the El Tatio hydrothermal region in northern Chile. The distribution of silica was mapped using previously reported spectral indices. The concentration of chlorophyll, a type of pigment produced or contained in many microbes, was mapped using the NDVI index.

Sinter samples exhibiting diverse macro- and microtextures were also collected from Puchuldiza-Tuja hydrothermal fields in northern Chile. These sinter samples were studied in the laboratory by various techniques, including SEM, micro-FTIR mapping, EPMA, and micro-Raman mapping.

Results and discussion: Here, we report the results of each technique and discuss the related implications.

Compositional remote sensing. Both ASTER and WorldView data were capable of effectively mapping the silica distribution and chlorophyll concentration in the hydrothermal region at El Tatio in Chile. Based on the WorldView data with a higher spatial resolution of up to 1.6-3.7 m/pixel, an apron morphology was reflected in the areas with high silica content. Thus, the high-resolution (~1 m/pixel) multispectral data are

helpful in determining the vent-to-distal apron geologic setting of a hydrothermal site.

In addition, more areas with high chlorophyll content were revealed in the NDVI mapping results applying the WorldView data, and they were concentrated in the vent or the distal apron in a hydrothermal system, the latter of which is more promising to find biosignatures.

High-resolution observations. Three thin sections and three polished bulk samples were studied.

The three thin sections displayed dense silica, laminations, and palisade textures, respectively. No microbial structures were visible in the dense silica and lamination sections under high-resolution observations, as laminations could be produced by biotic or/and abiotic processes. Palisade textures are micro-pillar microbial structures that are closely packed and bounded by upper and lower laminations [7]. In the studied palisade thin section, abundant microbial sheaths were observed under SEM.

The three polished bulk samples showed nodular grains, angular grains, and palisade textures, respectively. Microbial structures were found in all three samples under high-resolution observations.

Micro-FTIR mapping. Micro-FTIR mapping was collected on the three thin sections of sinter samples. The emissivity minimum of the silica in the dense silica sample was ~1090 cm⁻¹, while it was ~1100 cm⁻¹ in the palisade sample. For the laminated sample, the emissivity minimum ranged from 1083 cm⁻¹ to 1110 cm⁻¹. The lower shift of the emissivity minimum was caused by the substitution of AI for Si in hydrated silica, which was confirmed by EPMA analysis. Less AI substitution in sinters suggests fewer modifications by post-depositional processes and hence more opportunities to preserve biosignatures in sinter.

Overall, the emissivity minimum of the silica matrix containing no microbial structures shifted to a lower position than that of the silica matrix bearing microbial structures. Laminations could be produced by a combination of biotic and abiotic processes [8], which might be the reason for their wide range of emissivity minimum in the FTIR spectra.

Micro-Raman mapping. Micro-Raman mapping was conducted on all six samples. In our experiments, the fluorescence overwhelmed the Raman spectra when

employing a continuous green laser excitation (532 nm) on sinter samples [9]. Accordingly, a continuous red laser excitation (785 nm) was employed in this study.

No carbonaceous matter (CM) was identified in the thin section characterized by dense silica. CM failed to be identified in the laminated thin section possibly due to the fine laminations. CM was identified in palisade structures in both the thin section and the polished bulk sample, and the Raman spectra suggested CM in the palisades was very poorly organized. CM was also characterized in the other two polished bulk samples, while the distribution of CM was minor in both Raman mapping assessments.

Our results suggest that Raman spectroscopy may not work efficiently to identify carbonaceous matter in opaline silica sinter. When applying a continuous laser, a 785 nm setting may be more appropriate. More experiments with pulsed lasers are expected to be done in the future.

Conclusions: This study aims to provide refinements for identifying future astrobiological targets from the orbital perspective and the onsite spectroscopy perspective by studying silica sinters at El Tatio in northern Chile. Our results demonstrated that multispectral data with relatively higher spatial resolution could help determine the flow direction of discharging hydrothermal fluids on a planetary surface by estimating the amount of silica in the region. An instrument similar to the Miniature Thermal Emission Spectrometer (Mini-TES) on the *Spirit* rover is capable of providing information on emissivity minima in the TIR range, which gives an indication of silica chemistry and substitutions. Future Raman instruments allowing for multiple excitation lasers might be necessary for identification of biosignatures in silica-rich deposits from orbit.

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