SULFUR BIOSIGNATURES IN CONTINENTAL HOT SPRING, STREAM AND CRATER LAKE SEDIMENTS AFFECTED BY HYDROTHERMAL H_2S GAS EMISSION.

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Introduction: The major goal for the exploration of Mars in the coming decades is to determine whether life is, or was, present [1]. The Mars 2020 Rover will be “Seeking the Signs of Life” (e.g., biosignatures) through a broad and rigorous investigation using *in situ* instruments and archiving the most promising samples for potential return to Earth at a later time [1]. Our ability to successfully detect and interpret potential biosignatures of extant and/or extinct microorganisms on Mars can be improved by better understanding how well these biosignatures are preserved in geological record on Earth.

Sulfur (S)-bearing compounds are common on the Martian surface as sulfate and sulfide minerals[2]. The presence of S compounds on Mars has been mainly linked to hydrothermal activity in the past when Mars was more volcanically active and water was stable on the surface [2]. Similarly, gas- and dissolved-phase S-bearing compounds are abundant at modern volcanic systems on Earth, particularly continental springs where hydrothermal water discharges on land. These habitats support diverse microbial ecosystems that host metabolic guilds capable of S oxidation and reduction (i.e. redox reactions) for energy [3]. Therefore, investigating biosignatures associated with hydrothermal microbial S cycling on Earth is critical for identifying potentially similar biosignatures on Mars.

Goals & Research Approach: In this study, we focused on identifying two types of biosignatures in a continental volcanic complex of Valles Caldera, New Mexico:

1) *Metabolic ^{34}S-^{32}S isotope biosignatures* - characteristic imprints upon the environment of the processes by which life extracts energy and material resources to sustain itself.

2) *Molecular (genomic) biosignatures* - structural, functional, and information-carrying molecules that characterize life forms and their metabolism.

Between 2007 and 2014, water and sediment samples were collected from hot spring, stream and crater lake sediments affected by hydrothermal H_2S gas emission. The method of S sequential extraction was used to characterize isotope composition of mineral phases containing S^{6+}, S^0, and S^{2-} [4]. To link microbial metabolic potential with observed metabolic isotope signatures, we examined the presence of adenosine-5-phosphosulfate (APS) reductase, a gene involved in both dissimilatory (i.e. energy yielding) sulfate reduction or S oxidation reactions.

Results & Discussion: S isotopes have been used for interpreting modern and ancient metabolism because of large S isotope fractionations (~20 to 60‰) between oxidized (S^{6+}, S^0) and reduced (S^{2-}) species formed due to microbial sulfate reduction and disproportionation of elemental S [5]. In volcanic complex of Valles Caldera, biogenic sulfides with distinctive negative $\delta^{34}S$ of -40.3 to -9.9‰ were mainly preserved in stream sediments showing small and/or negligible hydrothermal H_2S emission. Conversely, in hot spring and stream sediments with high gas emission the $\delta^{34}S$ of sulfide minerals had higher values of -1.2 to +2.2‰ suggesting greater inputs of inorganic S from hydrothermal H_2S gas emission (+0.8 to +4.8 ‰). Molecular biosignatures were indicative of S-oxidizing acidophiles (*Desulfurella, Thiobacillus*) [6] and novel sequences related to both S oxidizers and reducers [this study] in hot spring and stream sediments. The $\delta^{34}S$ of sulfides from ancient crater lake sediments (~560 ka years) varied in a similar range (-3.9 to +4.0‰) as in the S-rich volcanic bedrock (-2.2 to +3.3‰) and modern hydrothermal H_2S gas. This, in turn, implies poor preservation of metabolic S biosignatures in lake sedimentary record resulting either from limited microbial S metabolism or complete microbial transfromation of oxidized S^{6+}/S^0 species to sulfides.

Looking for Biosignatures on Mars: The SuperCam instrument on the Mars 2020 Rover will measure elemental and mineralogical compositions during in situ investigation and collect samples for return to Earth. Generally, biogenic sulfides (metabolic biosignatures) with negative $\delta^{34}S$ showed very small content of <0.01 wt. S^{2-} % in the stream sediments of Valles Caldera and were below detection limit by Terra (XRD) Instrument. Also, DNA content (molecular biosignatures) was relatively low and challenging to extract from S-rich materials. Therefore, similar metabolic and molecular biosignatures on Mars could be only detected on the samples returned to Earth. Nevertheless, current orbital instruments such as HiRISE and CRISM could be used to detect potential hydrological drainage sites associated with hydrothermal H_2S activity and habitabile conditions, thus, guide the Mars 2020 rover for sample return collection.

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