

**$\Delta^{17}\text{O}$  OF MARTIAN SULFATE: ASSESSMENT AS A TOOL TO RECOGNIZE THE IMPACT OF BIOLOGICAL SULFUR CYCLING ON MARS.** B. Brunner<sup>1</sup> and M. L. Coleman<sup>2</sup>, <sup>1</sup>Astrobiology, JPL, Caltech 91109 Pasadena CA, Benjamin.Brunner@jpl.nasa.gov, <sup>2</sup>Astrobiology, JPL, Caltech 91109 Pasadena CA, Max.Coleman@jpl.nasa.gov.

**Introduction:** The Mars Rover-missions demonstrate that there are accessible Martian sulfate deposits (evaporites) [1]. These sedimentary rocks could indicate influence of past or present biotic processes even in the absence of traces of extraterrestrial life. We evaluate the potential of the analysis of mass independent isotope fractionation of oxygen in sulfate as a biosignature.

**Mass dependent isotope fractionation:** On Earth, biological sulfur cycling is important. Bacterial processes include sulfate reduction, sulfide oxidation and disproportionation of sulfur compounds. These enzyme-catalyzed reactions result in changes in the sulfur and oxygen isotope composition of sulfate. Due to intense biochemical sulfur-cycling, marine sulfate is enriched in <sup>34</sup>S compared to sedimentary sulfides and enriched in <sup>18</sup>O compared to the oxygen isotope composition of seawater. Also non-biogenic processes like thermochemical sulfate reduction and inorganic oxidation of sulfides contribute to the observed isotope patterns in marine sulfate. It is difficult to determine the relative importance of biogenic and nonbiogenic sulfur cycling.

**Mass independent isotope fractionation:** All isotope fractionations related to biogeochemical reactions are mass-dependent: The isotope fractionation is larger for isotopes with large relative mass differences, e.g. in a specific reaction, the fractionation effect for <sup>17</sup>O is roughly a half of the isotope effect for <sup>18</sup>O. However, photochemical processes do not obey mass dependent isotope fractionation and leave mass independent isotope signatures in sulfur compounds. A measure for such mass independent isotope signatures is the deviation of the mass independent isotope composition from the ratio that would be expected for mass dependent isotope composition. In the case of <sup>17</sup>O, this measure corresponds to the  $\delta^{17}\text{O}$  of a sample minus one half of the corresponding  $\delta^{18}\text{O}$  value ( $\Delta^{17}\text{O}_{\text{sample}} = \delta^{17}\text{O}_{\text{sample}} - 0.52 \times \delta^{18}\text{O}_{\text{sample}}$ ).

**Dilution of signature of mass independent isotope fractionation:** On Earth, such signatures of mass independent isotope fractionation processes are rarely observed.  $\Delta^{33}\text{S}$  values deviating from 0 have been observed in Proterozoic sulfides, indicating a partitioning between reduced and oxidized

atmospheric sulfur compounds. The observation that reduced sulfur compounds were not oxidized in the atmosphere implies that the Proterozoic atmosphere was oxygen poor.  $\Delta^{17}\text{O}$  values deviating from 0 have been observed in sulfate deposits from arid regions. In this case, a large part of the sulfate was derived from the atmosphere where photochemical mass independent isotope fractionation occurs. However, on Earth, most mass independent isotope signatures are erased by mixing of sulfur compounds with opposing mass independent anomalies (e.g. sulfides are rapidly reoxidized in the atmosphere and no partitioning between oxidized and reduced sulfur compounds can occur) or by dilution with sulfur compounds that do not have an imprint of mass independent isotope fractionation. The biologic sulfur cycle plays an important role in this process. It reduces potential  $\Delta^{17}\text{O}$  anomalies from sulfates by sulfate reduction (enables oxygen isotope exchange between water and sulfate) and oxidation of sulfur compounds, adding oxygen with no  $\Delta^{17}\text{O}$  anomaly.

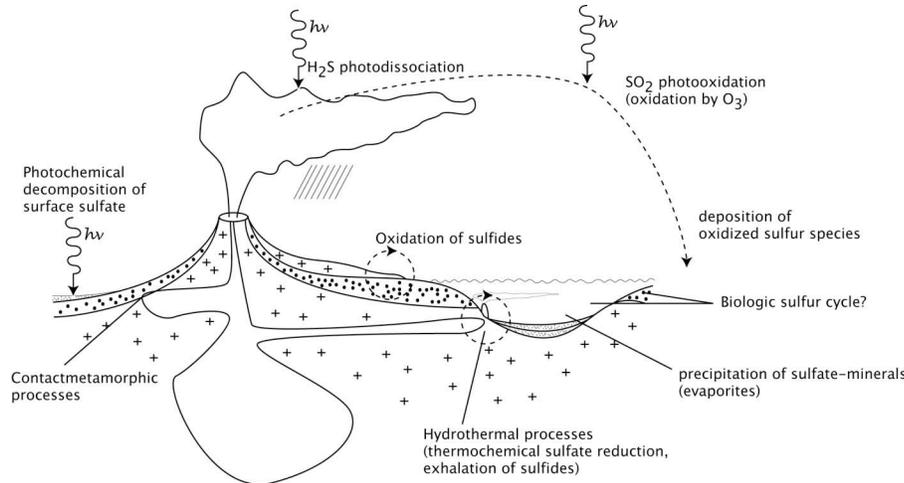
**Signature of mass independent isotope fractionation in Martian sulfate:** From meteorite studies Farquhar and Thiemens [2] concluded that <sup>17</sup>O mass independent isotope signatures in sulfate and in water may be much more abundant on Mars, the  $\Delta^{17}\text{O}$  signature of sulfate being different from the one of Martian water and oxygen. This raises the question if  $\Delta^{17}\text{O}$  of Martian sulfate can be used as a tool to detect biological sulfur cycling (Figure 1). Therefore, we evaluated the impact of various biogeochemical and photochemical processes on the sulfur- and oxygen isotope composition (i.e.  $\Delta^{17}\text{O}$ ) of Martian sulfate and summarized our results in a matrix (Table 1). This matrix allows us to draw conclusions how the sulfur and oxygen isotope composition and especially  $\Delta^{17}\text{O}$  signatures, of Martian sulfate can be interpreted. A box model demonstrates that  $\Delta^{17}\text{O}$  signatures of Martian sulfate could provide important information on the relative importance of (bio?)geochemical processes on Mars at the time of the formation of the sulfate minerals.

**Conclusions:** We come to the conclusion that stable sulfur and oxygen isotope analysis (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O and <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S) would significantly contribute to the understanding of the Martian geochemical water and sulfur cycle and that such data are a prerequisite detecting extraterrestrial

biogeochemical cycling of sulfur. The isotope composition of Martian sulfate traces the geochemical processes at the time of sulfate deposition. Thus, Martian sulfates are an archive of past and recent geochemical cycling on Mars. These findings emphasize the need to take an holistic and integrated approach to detecting life on Mars and the need to understand the geochemical cycle: a single component of it will not provide an unambiguous answer.

**References:**

[1] Squyres S. W. et al. (2004) *Science*, 306, 1698-1703. [2] Farquhar J. and Thiemens M. H. (2000) *J. of Geophysical Res.*, 105, 11991-11997. [3] Lee C. C-W. et al. (2001) *Geophysical Res. Letters*, 28(9), 11991-11997.



**Figure 1**

**Mars' exogenic sulfur cycle** (modified after Farquhar: [http://www.geol.umd.edu/~jfarquha/Farquhar\\_research.htm](http://www.geol.umd.edu/~jfarquha/Farquhar_research.htm)) Relative to (bio?)geochemical processes (mass dependent isotope fractionation), photochemical processes (mass independent isotope fractionation) might be much more important on Mars than on Earth. The mass independent isotope signature of sulfate derived from atmospheric processes is likely to be inherited from oxidants (O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) with mass independent isotope signature [3].

	Processes diluting the $\Delta^{17}\text{O}$ signature of sulfate derived from atmospheric oxidation of $\text{SO}_2$	Effect of mass dependent oxygen and sulfur isotope fractionation on $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of $\text{SO}_4$	
Abiotic oxidation of sulfides	$\Delta^{17}\text{O}$ signature inherited from oxygen source ( $\text{H}_2\text{O}$ , oxides)	small	small
Biotic oxidation of sulfides	$\Delta^{17}\text{O}$ signature inherited from oxygen source ( $\text{H}_2\text{O}$ , oxides)	large	small
Thermochemical sulfate reduction	$\Delta^{17}\text{O}$ signature inherited from oxygen source ( $\text{H}_2\text{O}$ , oxides)	large	large
Biological sulfate reduction	$\Delta^{17}\text{O}$ signature inherited from oxygen source ( $\text{H}_2\text{O}$ , oxides)	large	large
Photochemical decomposition of sulfate on regolith	?	small?	small?
Mixing of sulfate from different origin	$\Delta^{17}\text{O}$ signature inherited from oxygen source ( $\text{H}_2\text{O}$ , oxides)		
Hydrothermal release of $\text{H}_2\text{S}$ and removal of $\text{SO}_4$	$\Delta^{17}\text{O}$ signature inherited from oxygen source ( $\text{H}_2\text{O}$ , oxides)		
Precipitation of sulfate		small	small
Highly acidic conditions	$\Delta^{17}\text{O}$ signature inherited from oxygen source (water)	large	

**Table 1**

**Processes diluting the  $\Delta^{17}\text{O}$  signature of sulfate derived from atmospheric oxidation of  $\text{SO}_2$**