

REVIEW OF SULFATE SOURCES IN ANTARCTIC POLAR ENVIRONMENTS – GEOCHEMICAL IMPLICATIONS FOR SULFATE ORIGIN ON MARS. A. Szyrkiewicz¹, J. L. Bishop², and Z. F. M. Burton²,
¹Department of Earth and Planetary Sciences, University of Tennessee (Knoxville, TN; aszynkie@utk.edu), ²SETI Institute (Mountain View, CA).

Introduction: Determining aqueous sulfate sources and quantifying their contributions from chemical weathering and atmospheric deposition in terrestrial polar environments is important for understanding surface conditions and the sulfur cycle on Mars. A variety of sulfate minerals have been identified by rovers and orbital spectrometers in numerous locations on Mars [e.g., 1]. However, sources of sulfates in martian regolith and soils are poorly constrained. Most geochemical models are focused on coupled volcanically- and atmospherically-driven sulfur cycles, but cannot be solely explained by inputs from volcanic emission and atmospheric deposition [2]. Conversely, less emphasis has been placed on water interaction with primary sulfur-bearing minerals in the bedrock. So far, only a few studies have attempted to address whether chemical weathering (sulfide oxidation) could account for some of the sulfates detected on the martian surface [3-5]. One of the difficulties in addressing sulfate sources for Mars is limited research and no clear consensus on the sulfur cycle in terrestrial polar environments that are most analogous to Mars. While sulfide weathering is proposed to be the main sulfate contributor in Arctic glacial/subglacial systems [6], an atmospheric origin has been favored for sulfate accumulations under Antarctic dry polar conditions [7].

The main objective of this study is to critically evaluate chemical weathering and atmospheric processes that contribute to the formation of secondary sulfates in surficial deposits from different settings of the McMurdo Dry Valleys (MDV), Antarctica. The research goal is to quantify inputs of sulfates from chemical weathering and atmospheric deposition in MDV using stable isotope compositions.

Study Site: Although the MDV climate is cold and dry, and in many ways analogous to martian settings, liquid water occurs in lakes, ponds and streams with highly saline water during austral summers. Glaciation of Antarctica started ~65 Ma as a result of continental drift that moved Antarctica toward the South Pole. In the MDV, major glacial activity likely ceased by ~3-4 Ma in the valley bottoms, but there is also evidence that persistent cold-desert, ice-free and hyper-arid environmental conditions have existed in this region for up to ~8-11 Myr in the upland valleys.

Major rock formations outcropping on the surface are Paleozoic and Mesozoic sedimentary formations and basaltic lavas and dolerite sills. They are underlain by Precambrian basement rocks comprised of magmatic rocks and metamorphosed sedimentary and volcanic

rocks. Disseminated grains of pyrite are associated with several of these rock formations [8].

Methods: We performed sulfur sequential extraction and sulfur and oxygen isotope composition analyses on 8 sediment samples collected in 1980 [9] along the South Fork of Wright Valley (Fig. 1), including the main drainage area comprised of Don Juan Pond and VXE-6 Pond [10]. The sediments are from shallow depths (<1 to 20 cm) of then-dry, shallow-groundwater transient salt ponds and surface sediments. Isotopic analyses were performed using a Delta Plus XL mass spectrometer at the University of Tennessee. The analytical precision for both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ was <0.3‰.

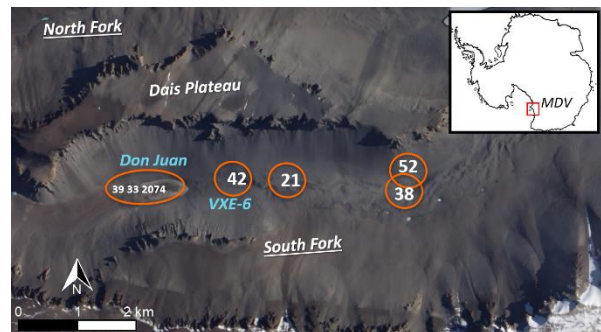
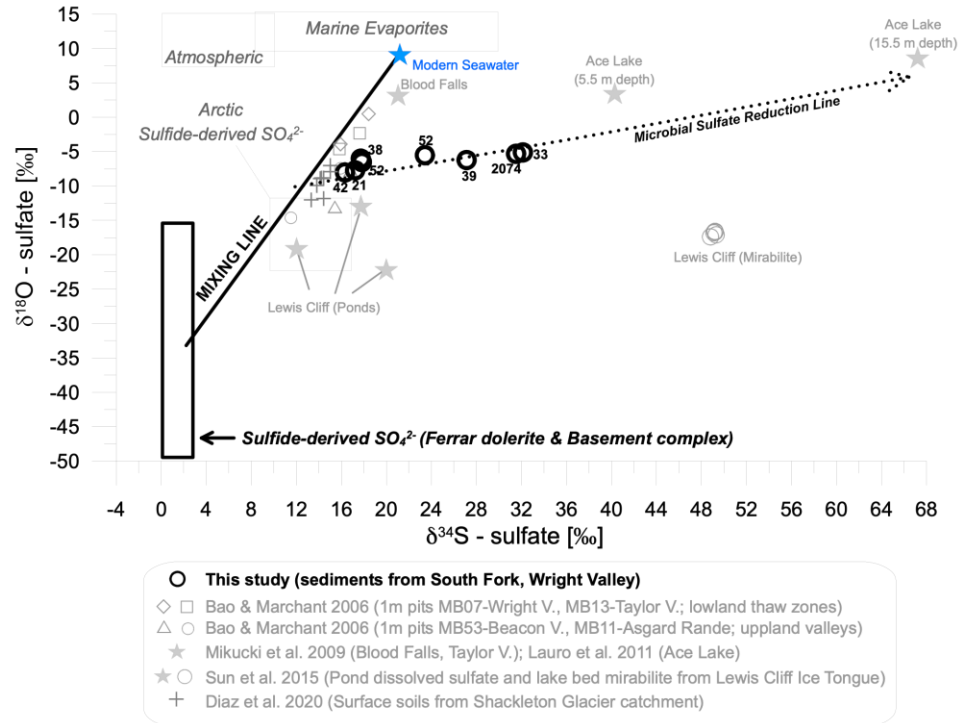


Figure 1. View of South Fork of Wright Valley showing locations of sampling points for isotope analysis.

Results: Along the studied portion of the South Fork catchment, the acid-soluble sulfate content was variable in soils (0.13 to 0.89 wt.% S), but significantly higher than the sulfide content (<0.01 wt.% S). The soil sulfate showed wider variation of $\delta^{34}\text{S}$ (+15.8 to +32.5‰) compared to smaller ranges of $\delta^{18}\text{O}$ (-8.9 to -4.1‰). The highest $\delta^{34}\text{S}$ values of sulfate were typically closest to Don Juan Pond (+27.1 to +32.5‰), while lower values occurred further upstream (+15.8 to +23.4‰). In contrast, the $\delta^{34}\text{S}$ of sulfide showed significantly lower and consistent values across the studied area (-0.6 to +3.3‰).

Conclusions: Our regional comparison of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate salts in Antarctic environments with new isotope results obtained via this study (Fig. 2) suggest significant contributions of sulfate from *in situ* sulfide oxidation in the bedrock and atmospheric deposition of sea aerosols. Additional sulfate inputs likely originate from subglacial brines derived by relicts of seawater and/or lake/pond water influenced by microbial sulfate

Figure 2. Comparison of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfates in surficial deposits, lakes and Blood Falls subglacial outflow of Antarctica with known atmospheric and marine sulfur endmembers. Black circles and sulfide-derived sulfate endmember are new isotope results for sediment samples from the South Fork of Wright Valley. In location 52, higher $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ were measured at depths of 2-4 cm and lower values at 4-8 cm.



reduction. Based on the $\delta^{34}\text{S}$ of bedrock sulfides in the South Fork of Wright Valley, sulfide weathering may contribute up to 20-50% of sulfate, despite relatively low sulfide contents in the bedrock (<0.01 wt.% S). However, the main question of actual contributions of sulfate from modern sea aerosols via atmospheric deposition and relicts of sea-or-lake waters trapped in subglacial environments remains. This cannot be easily quantified based on isotope compositions of sulfate using existing data sets, which are from samples rather randomly distributed across the MDV, and from limited bedrock analysis for $\delta^{34}\text{S}$. However, given that relict seawater in the MDV has elevated sulfate concentrations (~5,000 mg/L), we suggest that atmospheric contributions of sulfate might be minor, as previously estimated for wetter aqueous settings of the Northern Hemisphere (<5-10%). This would suggest that local sulfur endmembers activated by the hydrological cycle are the main sources for formation of secondary sulfate minerals under dry polar conditions, which is similar to alteration in glacial and subglacial systems in the Arctic.

Implications for Mars: Our isotope results imply that chemical weathering of pre-existing sulfide minerals in the bedrock is an important source of aqueous sulfate under extremely dry polar conditions with limited water activity. This finding is in good agreement with other terrestrial studies on the sulfur cycle in warmer and wetter climates, clearly pointing to the role of the hydrological cycle in remobilizing local sulfur endmembers that lead to formation of secondary sulfates in surficial sediments and soils.

A recent summary for the Meridiani Planum region by Hynek et al. [2] shows that the occurrence of sulfur-rich deposits cannot be explained using one sulfate source (e.g., volcanic emission, hydrothermal activity, or atmospheric). Similar conclusions can be drawn for other regions on Mars (North Pole, Valles Marineris, Gale), where one-source approaches have failed to address the complexity of sulfate occurrences relative to the accompanying chemical/mineralogical, sedimentary and geomorphological features. This is in agreement with S isotope analyses of martian meteorites [11]. As argued above, most terrestrial studies of sulfate budgets in aqueous settings point to multiple sulfate sources in aqueous settings: mainly from bedrock chemical weathering, with smaller proportions from direct volcanic/hydrothermal emissions and atmospheric deposition. We suggest that applying terrestrial models of sulfur cycles may help place better constraints on the origins of martian sulfates.

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