

ISOTOPIC ANALYSIS OF SALTS IN TERRESTRIAL HYPER-ARID DESERTS: ANALOGS FOR UNDERSTANDING THE ORIGIN AND MOBILITY OF SALTS ON MARS

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Introduction: The hyper-arid Atacama Desert and the McMurdo Dry Valleys (MDV) are excellent analog sites for understanding the origins and mobility of salts on Mars. Our group has been examining diverse soluble salts (e.g. SO_4^{2-} , NO_3^- , Cl^- , and ClO_4^-), particularly their multiple stable isotope compositions from terrestrial hyperarid surfaces. Past isotope analyses have revealed the sources of sulfate and examined translocation of salts in soils in the McMurdo Dry Valley's, as well as assessed the origin of perchlorate in the Atacama Desert. Aspects of this work should be further explored in light of recent results from the MER rovers and from the Phoenix Mars Lander.

Sulfate Sources: The sulfur and oxygen isotope compositions can reveal the origin of sulfate. The heterogeneity among oxygen and sulfur isotope compositions for sulfates on Earth attests to a dynamic and biologically active planet. The application of three isotope parameters, the $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$, has enabled quantitative determinations of the fractions of three sulfate end-members in soils of the McMurdo Dry Valleys (MDV) [1]. These results show a variable distribution of three end members in different microclimate zones of the valleys, revealing rich information on the fluxes and deposition of sulfate and their history. The apportionment is possible because the absence or near-absence of post-depositional sulfate reduction and because of a new parameter, the $\Delta^{17}\text{O}(\text{SO}_4)$.

Sulfate is known to be present in large quantity in Martian regolith. The sulfate budget on Mars may have two additional constraints, the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, that the Earth does not possess for modern surface environments. Thus, five potential parameters provide much better constraints on individual sulfate end-members when dealing with an inherently underdetermined system such as the mixture of *N* sulfate end-members on Mars.

Leaching Behavior: Similar to Mars, the MDV possesses surfaces where the normally rejuvenating actions of life, water, or ice are limiting. However, aeolian or atmospheric dust/salt accumulation and subsequent vertical migration are on-going processes that have not only altered the physical-chemical nature of the hyperarid surfaces but also recorded past environmental fluctuations during the hyperarid period. We have observed distinct leaching behavior

that is recorded not only by vertical soluble ion concentration profiles but also by the sulfate, nitrate, and chlorine isotope compositions [1,2].

Interpretation of hyperarid soil salt profiles has been contentious, and existing solute transport models for arid soil columns do not apply to the MDV where it is not only extremely dry but also extremely cold. It poses a series of questions on the ability of ion transport by brine at extremely low temperature. Correctly modeling these profiles is important, as their interpretation has significant consequences on our understanding of both MDV and Martian surface histories. Preliminary modeling has qualitatively reproduced the observed concentration profiles by treating ion transport as a function of both the magnitude and the frequency of wetting events.

Perchlorate Puzzle: Perchlorate (ClO_4^-) is a minor component of the hyperarid Atacama Desert salts, and its origin has long been a subject of speculation. Our study has firmly established its atmospheric origin [3]. The evidence came from the measurement of triple-oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$) of both man-made perchlorate from commercial sources and natural perchlorate extracted from the Atacama soils. Only the Atacama perchlorate bears an ^{17}O anomaly. However, the small data set exhibits two intriguing observations that demand further study: (1) Both the $\delta^{18}\text{O}$ and $\delta^{37}\text{Cl}$ for the Atacama perchlorate is rather negative, hinting a fundamentally different photochemical pathway(s) from that of atmospheric nitrate (NO_3^-), and (2) the positive ^{17}O anomalies are variable (from +4.2 to +9.6‰). These results indicate a deficiency in the understanding of Cl cycle and demands the investigation of the unknown alteration process.

While perchlorate is easily detectable in soil of the Central Depression (the driest part of the Atacama Desert), its presence in the MDV soils is curiously low or undetectable. Perchlorate was detected by the Phoenix Mars Lander on Martian regolith. Understanding perchlorate's origin in hyperarid surfaces on Earth should provide the best clue for its origin on Mars.

References: [1] Bao, H and Marchant, D. (2006) *JGR*, **111**(D16). [2] Bao, H. et al (2008), *JGR*, **113**(D3). [3] Bao, H. and Gu, B. (2004), *Environ. Sci. & Tech.* **38**(19), 5073-5077.