

SULFATE'S TRIPLE-OXYGEN ISOTOPE HYDROGEOCHEMISTRY. Huiming Bao^{1*}, Xiaobin Cao¹, and Yongbo Peng¹, ¹Department of Geology & Geophysics, E235, Howe-Russell-Griffin Geosciences Complexes, Louisiana State University, Baton Rouge, LA 70803, USA (*bao@lsu.edu).

Sulfate is an ion ubiquitously present on Earth today. Oxidative weathering and evaporite dissolution constitute two of the most important sources of dissolved sulfate in ground and surface waters. Other minor sources include atmospheric secondary sulfate deposition and fertilizer application. Each of the sources has their characteristic sulfur and oxygen isotope compositions, and the $\delta^{34}\text{S}$ and increasingly in combination with its associated $\delta^{18}\text{O}$ are used to decipher the sources and formation pathways of river and groundwater sulfate. Assisted by ion chemistry data, the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulfate often reveal the chemical processes and degree of weathering in a river basin or a groundwater system. Despite the resolving power of the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, ambiguities remain on the source partition due largely to overlapping parameter ranges for end-members. In past two decades, theoretical and analytical advancement in sulfate triple-oxygen and quadruple-sulfur isotope compositions, i.e. the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ or $\Delta^{17}\text{O}$ for oxygen and the $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ for sulfur, has provided us higher-dimensional parameters to further resolve the origin of sulfate in diverse Earth environments. In particular, sulfate records from the distant past have uncovered very different Earth atmosphere-biosphere-hydrosphere systems, so different that these past systems may well be treated as different planet conditions.

A recent study on the Mississippi River basin (MRB) has shown that there are resolvable differences in triple-oxygen isotope compositions of the dissolved sulfate [1]. While parameter $\Delta^{17}\text{O}$ does add a new perspective, a clear interpretation was hindered by a lack of reference frames in $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space, which is essential when the $\Delta^{17}\text{O}$ range is small relative to measurement resolution. Here we synthesized, statistically treated the published sulfate triple-oxygen isotope data and constructed end-member ranges in $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space for sulfate derived from sulfide mineral oxidation today and for evaporite sulfate of the Ediacaran Period and Phanerozoic Eon. The defined 2-D space encompassed nearly all the MRB data and offered a visually straightforward way of interpreting sulfate source partition and origins. When placing the modern hydrogeochemical $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space in the broader sulfate $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space defined by data throughout the 3.8 billion-year geological records, we see the data today representing a snapshot of an evolving Earth system (Fig. 1).

The constructed sulfate $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space here can be applied to studying potentially diverse sulfate end-members on Mars. In the meantime, to confirm the validity of the $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ 2-D range for sulfate derived from sulfide oxidation, we must calibrate a few critical parameters during sulfide oxidation processes, including the θ (the triple isotope exponent) value for equilibrium sulfite-water exchange and the KIEs and θ_{KIE} for sulfite oxidation to sulfate.

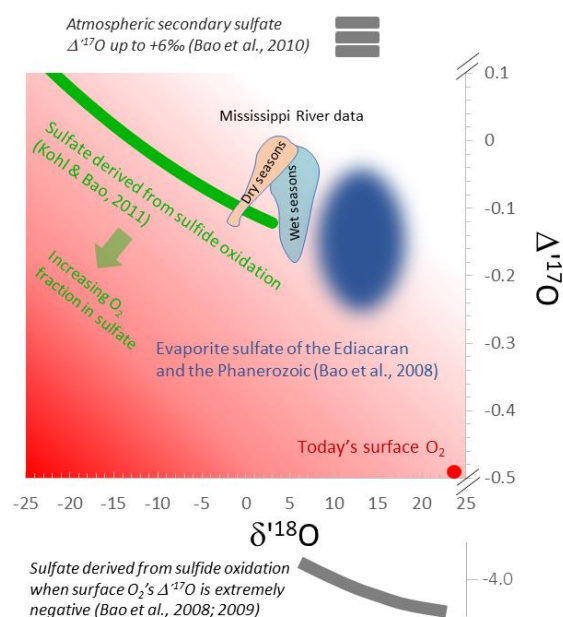


Fig. 1. Major sulfate end-members in $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space, modern and geological times.

References: [1] Killingsworth B. A., Bao H., and Kohl I. E. (2018) *Environ. Sci. Technol.*, 52, 6126–6136. [2] Bao H., Lyons J. R., and Zhou C. (2008) *Nature*, 453, 504–506. [3] Bao H. et al. (2009) *Science*, 323, 119–122. [4] Bao H., Yu S., and Tong D. Q. (2010) *Nature* 465, 909–912.