

Sulfate triple-oxygen isotopes from microbially catalyzed pyrite oxidation carry an extreme kinetic isotope effect associated with atmospheric oxygen incorporation

ISSAKU E. KOHL¹, NILS J. KULHUSCH², BRYAN A. KILLINGSWORTH³, KAREN ZIEGLER⁴, EDWARD D. YOUNG⁵ AND MAX COLEMAN⁶

¹University of Utah

²Thermo Fisher Scientific (Bremen) GmbH

³U.S. Geological Survey, Geology, Energy & Minerals Science Center

⁴University of New Mexico Institute of Meteoritics

⁵University of California, Los Angeles

⁶NASA Jet Propulsion Laboratory

Presenting Author: issaku.kohl@utah.edu

Microbial pyrite oxidation, ubiquitous in acid mine drainage (AMD) environments, may have been significant on the ancient Terrestrial and Martian surface but diagnostic tracers are needed. To this end, we examine labeled and natural abundance triple-oxygen isotope data for sulfate produced via pure culture microbial pyrite oxidation along with abiotic controls and natural data from the Río Tinto, Spain, AMD site. Sulfate from Río Tinto and our experiments contain a unique kinetic triple-oxygen isotope mass fractionation effect (β) associated with microbial lag phase pyrite oxidation by *Acidithiobacillus ferrooxidans* (*Af*) (Figure 1). Lag phase pyrite oxidation proceeds via the direct nucleophilic attack of O_2 on the sulfur site of pyrite and the β is statistically distinct (Z-test, 95% confidence) from sulfate produced by abiotic controls and the *Af* exponential growth phase, where *Af* facilitates indirect oxidation by producing Fe^{3+} , resulting in H_2O -oxygen incorporation in sulfate (Figure 2). These results indicate that in addition to containing signals from water and air, sulfates can also contain a biosignature that may be identified by its unique β .

Current kinetic isotope effect models do not include β values required to explain the triple-oxygen isotope data presented here, due to SO_3^{2-} - H_2O oxygen exchange dominating SO_4^{2-} oxygen isotope compositions. This reveals the need to better understand intermediate reaction chemistry preceding SO_3^{2-} formation and subsequent oxidation. We favor a mechanism wherein thiosulfate disproportionation produces S^0 , which is subsequently oxidized by dissolved atmospheric O_2 . Regardless of the exact mechanism, further observations via direct triple-oxygen isotope measurements of intermediates by Fourier-transform isotope ratio mass spectrometry are needed to better explain how >80% oxygen from air O_2 could be incorporated into sulfate in extremely low pH environments and how these chemical conditions persist for decades in the Río Tinto without transitioning to an Fe^{3+}/H_2O dominated system.

