

A sulfur four-isotope signature of Paleoarchean metabolism. K. W. Williford^{1,2}, T. Ushikubo^{2,3}, K. Sugitani⁴, K. Lepot^{2,5}, K. Kitajima², K. Mimura⁴, J. W. Valley² ¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109 USA ²WiscSIMS, Dept of Geoscience, University of Wisconsin, Madison, WI 53706 USA, ³Kochi Institute for Core Sample Research, JAMSTEC, Nankoku, Kochi, Japan ⁴Dept of Environmental Engineering and Architecture, Nagoya University, Nagoya 464-8601, Japan, ⁵Université Lille Nord de France, Lille 1, Laboratoire Géosystèmes, CNRS UMR8217, 59655 Villeneuve d'Ascq, France.

Introduction: When the disappearance of so called “mass independent” fractionation of sulfur isotopes (S-MIF) at ~2.4 Ga was first interpreted to indicate pervasive atmospheric oxidation, a supporting observation was the correlation between $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ with a slope of -0.9 that has come to be known as the “Archean array” [1]. The consistency of this relation through the Archean sulfur isotope record has been interpreted to represent consistency in the atmospheric process(es) responsible for generating S-MIF, and conversely, slight shifts in slope (e.g. to -1.5) recently observed in some Neoproterozoic rocks have been interpreted to result from changing atmospheric chemistry [2]. High precision sulfur four-isotope analysis of Phanerozoic sedimentary sulfide (e.g. in a Jurassic pyritized ammonite) indicates a $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ slope of -6.9 with $\Delta^{36}\text{S}$ as low as -2.40‰, interpreted to result from a cascade of mass-dependent enzymatic effects during sulfur metabolism [3]. Here we report new data from spatially resolved, in situ sulfur four-isotope analysis of pyrite from microfossiliferous samples of the ~3.4 Ga Strelley Pool Formation using secondary ion mass spectrometry (SIMS) [4]. Our data suggest a new kind of sulfur isotopic biosignature and support previous reports of Paleoarchean sulfur metabolism.

Methods and Results: A total of 115 SIMS sulfur three- and four-isotope measurements were made of individual pyrite grains in two microfossiliferous chert samples from the Waterfall Ridge locality and one sample from the Anchor Ridge locality of the Strelley Pool Formation. Data from pyrite grains in Neoproterozoic shales and carbonates measured during the same analytical session [5] are included for comparison. Sulfur three-isotope measurements were made using the WiscSIMS CAMECA IMS 1280 with a ~10 μm -diameter beam, and sulfur four-isotope measurements with a ~20 μm -diameter beam at the same facility.

Discussion: Three distinct categories of pyrite were observed in the three samples: 1) euhedral pyrite in the Waterfall Ridge samples, commonly associated with veins, 2) framboidal pyrite in Waterfall Ridge samples, in at least one case overgrowing a kerogenous microfossil, and 3) anhedral pyrite with possible dissolution textures in the Anchor Ridge sample that may represent degraded framboids. Euhedral pyrite grains from Waterfall Ridge have $\delta^{34}\text{S}$ between 0 and -15‰

(VCDT), and they are close to the origin on the $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ plot, perhaps indicating a hydrothermal source of sulfide decoupled from atmospheric interaction. Anhedral pyrite grains from the Anchor Ridge locality show a similar lack of S-MIF and a very small range of $\delta^{34}\text{S}$ (0 to -4‰), and may indicate a metasomatic overprint. Framboidal pyrite from the Waterfall Ridge locality is better preserved and exhibits a heretofore unreported range of sulfur four-isotopic compositions. These pyrite grains vary between -2 and 10‰ in $\delta^{34}\text{S}$, are uniformly positive in $\Delta^{33}\text{S}$ (0.7 to 2‰), and range from -5 to -14‰ in $\Delta^{36}\text{S}$ along a slope (-7.6) similar to that previously observed in Phanerozoic pyrite that likely resulted from microbial sulfate reduction (-6.9). These observations are consistent with a complex metabolic sulfur cycle in the Paleoarchean dominated by early diagenetic disproportionation of zero valent sulfur preserved in framboidal pyrite at the Waterfall Ridge locality that escaped later sulfur mobilization evidenced by euhedral pyrite and dissolution textures at Anchor Ridge.

References: [1] Farquhar, J. et al. (2000) *Science*, 289, 756–758. [2] Zerkle, A. et al. (2012) *Nat. Geosci.*, 5, 359–363. [3] Ono, S. et al. (2006) *GCA*, 70, 2238–2252. [4] Ushikubo, T. et al. (2014) *Chem. Geol.*, 383, 86–99. [5] Williford, K. et al. (in revision)

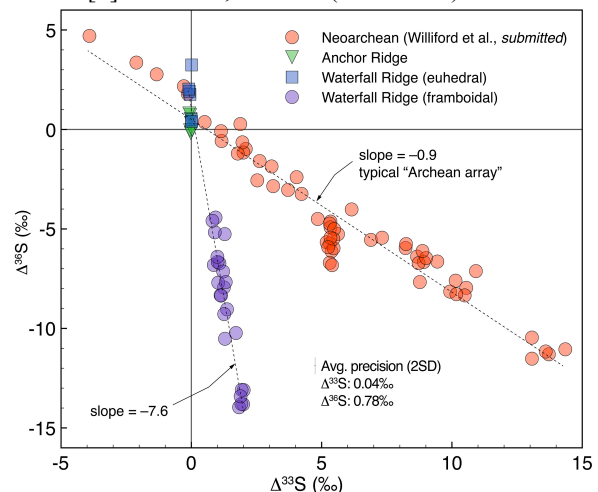


Fig. 1. SIMS sulfur four-isotope measurements of euhedral and framboidal pyrite in the microfossiliferous Paleoarchean Strelley Pool chert (this study) and Neoproterozoic shales and carbonates [5].