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M N
Q H_2 F I

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Uncovering primary microbial byproducts from sedimentary archives is critical for exploring the coupled evolution of life and the Earth surface system. Multiple sulfur (S) isotope measurements have provided important constraints on the vigour and emergence of different S-based metabolisms in ancient biospheres. However, previous studies have relied upon mineral-based isotopic records, requiring the untested assumption that the translation of microbial byproducts to the sedimentary mineral record is isotopically unimportant.

To address this issue, we designed a new method to measure the multiple S isotope composition of H_2S in fluid inclusions at nanomolar quantities. This method involved crushing samples under vacuum and purifying liberated gas through cryo-focusing steps. $H_2S_{(g)}$ was then converted to $Ag_2S_{(s)}$ via direct sulfurization onto Ag mesh or foil. Samples were then converted to $SF_{6(g)}$, purified, and introduced to an isotope ration mass spectrometer via micro-volume. We then applied this method to ≈3.5 Ga barites from Western Australia. Results yielded consistently negative $\Delta^{33}S$ values and larger $\delta^{34}S$ isotopic fractionations between reduced and oxidized forms of S than has previously been documented in Paleoarchean samples. Our results provide further evidence that dissimilatory sulfate reduction drove the Paleoarchean S cycle, and that mineralogical records preserve a slightly diminished isotopic signal of this metabolism.