

Multiple Sulphur Isotope Studies of Pyritised Microbialites from the Neoarchaeon Ghaap Group, South Africa

N. R. MEYER*¹, A. L. ZERKLE¹, D. A. FIKE²

¹DEES, Univ. of St. Andrews, KY16 9AL, UK

(*correspondence: nrm6@st-andrews.ac.uk)

²EPS, WashU in St. Louis, MO 63130, USA.

Multiple sulphur isotope studies are powerful proxies to understand the complexity of S biogeochemical cycling in the geological past. Iconically, the disappearance of a Sulphur Mass Independent Fractionation (S-MIF) signal in rocks younger than ~2.4-2.3 Ga has been used to date a dramatic rise in atmospheric oxygen in the Palaeoproterozoic. However, intricacies of the sulphur cycle before the Great Oxidation Event remain poorly understood. For example, the isotope composition of coeval elemental sulphur and sulphate is still debated. Furthermore, the variation in $\delta^{34}\text{S}$ in Archaean pyrite has been widely attributed to microbial sulphate reduction (MSR), although textural evidence for the presence and distribution of sulphate reducers remains enigmatic.

We combined detailed petrographic and high-resolution multiple S-isotope studies ($\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$) using Secondary Ion Mass Spectrometry (SIMS) to document the S-isotope signatures of exceptionally well-preserved, pyritised microbialites in shales from the ~2.65 Ga Lokammona Formation, Ghaap Group, South Africa. The presence of MSR in this Neoarchaeon microbial mat is supported by: a) textural evidence, including biogenic wavy crinkled laminae, and b) early-diagenetic pyrite containing μm -scale variations in $\delta^{34}\text{S}$ of 0 to +27‰ and $\Delta^{33}\text{S}$ variations of -2 to +2‰. These large variations in S isotope values suggest Rayleigh distillation of a limited sulfate pool during high rates of MSR in the microbial mat. Furthermore, we identified a second, morphologically distinct pyrite phase that precipitated post-lithification, with a $\Delta^{33}\text{S}$ signature of +6‰. We propose that the S-MIF signature of this late-diagenetic pyrite does not reflect contemporaneous atmospheric processes at the time of deposition; instead, it formed later by magnetic isotope effects during thermochemical sulphate reduction, and/or the dissolution and reprecipitation of older pyrite containing an atmospheric S-MIF signal. These insights provide new understanding of pyrite formation over several generations, and highlight the complimentary nature of petrography and SIMS studies to distinguish between pyrite phases in the geological record.