**Microbialites micropyrite: A pristine time capsule of microbial sulfate reduction throughout the geological**

J. Marin-Carbonne1, M.N. Decraene1, L. Remusat2, R. Havas3, V. Pasquier5, J. Alléon1, S. Bernard, N. Olivier, N. Zeyen6, A. Bouton3, S. Escrig7, E. Vennin3, A. Meibom7,1 and K. Benzerarra2, C. Thomazo3,4

Microbial mats are laminated layers of diverse microbial communities that exist across strong geochemical and redox gradients. The relationships between the diverse microbial metabolic activities and the isotopic signatures in associated biominerals formed in these mats are key to understand the modern biogeochemical cycle(s), but also to interpret the geological record. While previous studies have documented in detail the locus of sulfate reduction processes, through identification of soluble sulfur species captured using silver disks, very few have analyzed individual pyrite grains present within the microbial mats. Here we present detailed mineralogy coupled with NanoSIMS analyses of pyrites S-isotopes, reported as Δpyr (i.e. Δpyr ≡ δ34SSO4 - δ34Spyr) in two different microbialites, from the Cayo Coco hypersaline lake (Cuba) and from the Atexcac alkaline lake (Mexico).

These continental and marine settings bear different water chemistries, including strong differences in sulfate concentrations. Each of the investigated microbialites from both localities contain two distinct pyrite morphologies: 1) framboids, with sizes ranging from 2 to 15 m, and 2) euhedral micropyrites not exceeding 3 µm in size. Textural observations by electron microscopy suggest that the latter precipitated syngenetically during lithification, while framboidal pyrite precipitated earlier at the water-sediment interface or directly within the water column. Framboids displayed 34S values ranging from -45 to -10 ‰ (average of -19.5 ± 5‰ and -26.1 ± 6‰, 2SD for Cayo Coco and Atexcac, respectively), while micropyrites had more variable and lighter sulfur isotopic compositions with 34S between -86 to -17 ‰ (average of -34.5 ± 29 ‰ and -61.3 ± 17‰, 2SD for Cayo Coco and Atexcac, respectively). Moreover, individual framboidal pyrites show a distinct trend of 34S values from core to rim suggesting isotopic Raleigh distillation during their growth. Considering the sulfate isotopic composition associated with both environments, micropyrites display a similar range of Δpyr (i.e. Δpyr ≡ δ34SSO4 - δ34Spyr) from 56 to 62 ‰. These measured Δpyr values are consistent with an equilibrium fractionation observed in natural settings at low microbial sulfate reduction respiration rates. These results highlight the potential of micropyrites to capture signatures of microbial sulfate reduction and confirm that S isotope composition in pyrites record local microenvironments. Overall, this challenges the robustness of using bulk Δpyr for reconstructing secular evolution of S biogeochemical cycle through Earth history.