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Importance of nanoscale analyses for the measurement of sulfur isotope ratios and the distribution of trace elements in modern sedimentary pyrite framboids

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Pyrite (FeS_2) formed in sedimentary environments serves as an important sulfide mineral due to the inclusion of trace elements (TEs) providing insight into paleoclimate. In addition, the result of sulfur isotope ratios offers details on the evolution of ocean redox. Together, TE abundance and sulfur isotopes can be used to reconstruct early conditions on Earth and better understand periods of ocean anoxia [1]. TEs in marine systems can be held in the structure of pyrite framboids (spherical clusters of microcrystals), and their distribution at the nanoscale provides context for the timing and dynamics involved in incorporating a given element. Open vs. closed system dynamics can also be determined by ratios of sulfur isotopes, as framboids forming in an open system are isotopically lighter than the original sulfate (energetically favourable for sulfate reducing bacteria to utilize ^{32}S) [2]. Recently, transmission electron microscopy and atom probe tomography analyses from the Cariaco Basin and the Demerara Rise have shown that there is significant variation of TEs in different parts of pyrite framboids [3,4]. The relative timing of this later TE enrichment and its relation to S-isotope ratios is unknown. Further research into heterogeneities in TE distributions and sulfur isotope concentrations may provide detail not only about the formative settings, but the enrichment events that make up the formation of a framboid.

In this study, sediment samples were taken from two sites located in Saanich Inlet (Vancouver Island, BC) – a seasonally anoxic fjord – as the cyclic nature of the site results in chemically distinct conditions over a relatively short period of time. On average, framboids are <10 µm in size, making nanoscale analyses critical to observe variations within a single framboid, indicative of distinct periods of growth. This study employed the use of nanoSIMS and APT to observe the distribution of TEs at the microscopic to nanoscopic scale and measure sulfur isotope ratios.

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