

# Importance of nanoscale analyses of sulfur isotopes on the formation of pyrite framboids

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In marine ecosystems, pyrite (FeS<sub>2</sub>) forms as spherical clusters of microcrystals, but the exact mechanisms of formation are poorly understood. Studies have shown these clusters, or framboids are capable of recording water column chemistry of their environment. In low oxygen conditions sulfate (SO<sub>4</sub><sup>2-</sup>) is utilized instead of O<sub>2</sub> for respiration, producing H<sub>2</sub>S which is ultimately incorporated in sulfide minerals, predominantly pyrite. As this pyrite forms in an open system, it is significantly lighter than the original sulfate, as it is energetically favourable to use the lighter isotope (<sup>32</sup>S). Studies have also shown that S-isotope fractionation is related to the rate of reduction, and low rates using H<sub>2</sub> exhibit lower fractionations [1]. Differences in isotope concentrations may provide detail not only on the formative environments, but the types of microorganisms that may have been present at a given time. This makes the study of S-isotopes extremely important for analyses of anoxic ocean sediments and the evolution of S metabolism [2]. Recently, TEM analyses by Gregory et al., (2022, *in press*), from the Cariaco Basin and the Demerara Rise have shown that there is significant variation of trace elements in different parts of pyrite framboids. The relative timing of this later trace element enrichment and its relation to S-isotope ratios is unknown.

In the present 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 provided 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 periods of growth. This study employed the use of nanoSIMS to identify heterogeneity in S-isotopes within and between pyrite framboids to better understand the mechanisms involved in their crystallization. Results will be discussed through the comparison of different sizes and shapes of framboids found at varying sediment depths from the two sites.

References:

[1] Kaplan & Rittenberg (1964), *Journal of General Microbiology* 34, 195–212.

[2] Shen, Buick & Canfield (2001), *Nature* 410, 77–81.