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Pyritic event beds and sulfidized Fe (oxyhydr)oxide aggregates in organic-rich black mudstones of the Paleoproterozoic Talvivaara formation, Finland

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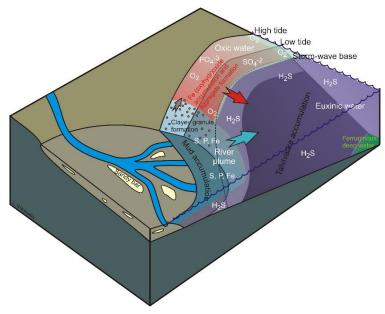
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The Paleoproterozoic, 2.0–1.9 Ga Talvivaara formation of Finland was deposited during the Shunga Event, a worldwide episode of enhanced accumulation of organic-rich sediments in the aftermath of the Lomagundi–Jatuli carbon isotope excursion. Sulfidic carbonaceous mudstones in the Talvivaara formation contain one of the largest known shale-hosted Ni deposits.

To gain new insight into this Shungian sedimentary environment, sedimentological, petrographical and *in situ* S and Fe isotopic microanalyses were carried out on samples representing depositional and earlydiagenetic conditions [1]. The event-bedded lithology with tidal signatures in the organic-rich mudstones strongly indicates deposition from predominantly river-delivered mud on a highly-productive coastal area, below storm-wave base. The riverine supply of phosphorus, sulfate and iron supported high primary productivity and resulted in strong lateral and vertical chemical gradients in the nearshore waters with a shallow oxic surface layer underlain by euxinic water. The stratigraphic upper part of the Talvivaara formation contains banded intervals of thin alternating pyrite beds and carbonaceous mudstone beds. The pyrite beds were deposited by seaward excursions of the concentrated, acidic Ferich river plume subsequent to droughts or dry seasons, which led to intense pyrite precipitation upon mixing with euxinic waters. δ^{34} S and δ^{56} Fe values of the bedded pyrite (median δ^{34} S = -10.3‰ and δ^{56} Fe = -0.79‰) are consistent with the reaction of dissolved Fe(II) with H₂S from bacterial sulfate reduction. Organic-rich clayey Fe-monosulfide-bearing granules were transported from the muddy estuary, and enclosed in Fe (oxyhydr)oxide aggregates that were forming by wave and current reworking in nearshore accumulations of river-delivered iron. The isotopic composition of these presently pyrrhotitic



inclusions (median $\delta^{34}S = -3.3\%$ and δ^{56} Fe = -1.6‰) indicates microbial iron The reduction. Fe (oxyhydr)oxide aggregates were transported in muddy debris flows to the distal euxinic seafloor. Their Fe (oxyhydr)oxide matrix was replaced by pyrite (median $\delta^{34}S$ = +5.8‰ and δ^{56} Fe = +0.81‰) at shallow sediment depths with ³⁴S and ⁵⁶Feenriched porewater. Wavv-crinkly laminae of possible microbial origin developed on the euxinic seafloor during low sedimentation.

Figure 1: Summary diagram of sedimentary environment.

These results indicate episodic deposition at seasonal to multiannual time scales. δ^{34} S and δ^{56} Fe values in the studied Fe-sulfides provide evidence of microbial isotope fractionation and syndepositional and early-diagenetic origin, finding no support for the previously proposed local hydrothermal activity in the Talvivaara mudstones.

References:

[1] Virtasalo JJ et al. (2015) Earth and Planetary Science Letters 432:449-460.