Seasonal redox oscillation and OC enrichment in a cold-climate organic rich rock

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The geological record identifies a strong bias toward organic carbon (OC) rich shales accumulating during greenhouse periods and OC that is intimately associated with fine-grained, chemically mature sediments. Permo-Carboniferous marine sediments in the Arckaringa Basin of Southern Australia, however, are an exception with anomalously high OC concentration of up to 11% TOC occurring within mineralogically immature siltstones that were deposited in deep, marine fjords in a proglacial setting. OC is hydrogen rich and occurs as discrete particles. Unlike many black shales deposited under greenhouse conditions, there is no relationship between TOC and mineral surface area, indicating a different mechanism of preservation

Electron imaging and energy dispersive X-ray (EDX) microanalysis reveal an association between organic carbon rich laminae and high sulphur concentrations, occuring both bound to OC and in the form of framboidal pyrite. Pyrite and OM rich laminae alternate with organic poor laminae featuring abundant manganese carbonate (kutnohorite) at mm scales, forming cyclical deposits interpreted as varves. These couplets identify the seasonal oscillation of water column redox conditions with pyrite deposition indicating euxina whereas freshening results in precipitation of dissolved Mn to form kuthnohorite.

We attribute OC and pyrite enrichment to stratification in the ancient fjord, leading to H_2S build up followed by mixing and bottom-water ventilation following seasonal temperature change, or longer term changes in sill height influencing restriction. The reducing conditions of the fjord provided a chemical trap for Mn and S from seawater sulfate. Excess dissolved sulphur in the water column and sediment pores promoted the preservation of H-rich, labile organic matter. By contrast, OC in kutnohorite rich laminae is mainly refractory terrigenous OC, consistent with limited preservation of labile marine OC due to improved bottom-water ventilation. Sulfurization reactions were thus critical for OC preservation and were facilitated by restriction in the ancient fjord.