

Mo and Os as indicators of atmospheric oxygenation: evidence from Paleoproterozoic black shales at Talvivaara, eastern Finland

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Compared to average continental crust or average shale, black shales are generally enriched in several redox-sensitive elements, such as U, V, and Mo, making them useful indicators of redox conditions in marine settings and indirect indicators of atmospheric evolution. We have studied the geochemistry of black shale samples from the Kuikkalampi Formation, which lies above the Talvivaara Ni-Zn-Cu-rich black shale unit in eastern Finland (Kontinen & Hanski 2015; In: Mineral Deposits of Finland, Elsevier, p. 557-612.). These black shales were deposited ca. 1.90–1.93 Ga ago and thus postdate the beginning of the Great Oxygenation Event by several hundreds of millions of years.

The Mo contents of the analyzed Kuikkalampi Fm samples are very high, averaging 167 ppm and reaching values up to 326 ppm, thus clearly exceeding the world black shale median of 20 ppm. Similar levels are normally only found in some Phanerozoic black shales. Mo correlates well with U and C_{org} and occurs as tiny molybdenite flakes in close association with carbonaceous nodules 0.01–0.2 mm in size. We analysed several molybdenite-bearing light mineral fractions for Re-Os isotopes, yielding an isochron with an age of 1848 ± 18 Ma, which likely represents a time of meta-morphic re-equilibration. After correcting for isotopic evolution between 1.92 and 1.85 Ga, a radiogenic initial $\gamma_{Os}(1.92 \text{ Ga})$ value of ca. +220 is obtained.

Exceptionally high Mo contents and elevated initial γ_{Os} of the Kuikkalampi Formation black shales suggest an elevated Mo content and radiogenic Os isotopic composition of sea water at 1.92 Ga, due to oxidative weathering of sulfides in exposed Archean and Paleoproterozoic crust. Modern analogues suggest operation of a particulate Mn-Fe-oxyhydroxide shuttle in a weakly restricted anoxic depositional basin during the black shale deposition.