

Trace metal enrichment in 1.98 Ga black shales of the Zaonega Formation

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Objective

Trace metal enrichment and isotopic composition in black shales are frequently used tools for estimating both local and global marine redox conditions. Large-scale studies of redox sensitive metals, such as Mo and U, show a characteristic peak in their abundance around the time of the Great Oxidation Event and subsequent Lomagundi Excursion (2.45 to 2.0 Ga), thought to result from the onset of oxic weathering on land. A decrease in atmospheric O₂ levels together with an increase in ocean euxinia has been inferred starting at roughly 2.0 Ga, and corresponds to a decline in trace metal enrichment [1]. It remains unresolved, however, to what extent these trends are affected by basinal rather than global conditions.

We have analyzed trace metal concentrations and isotope systematics in a 100 m section of the 1.98 Ga Zaonega Formation (ZF). This allows us to assess the importance of basinal versus global signals on trace metal enrichment and to provide a window into the second major redox transformation of the Paleoproterozoic, which paved the way for the low-O₂ world of the Mesoproterozoic.

Materials and methods

The ZF, NW-Russia (Fig. 1) is a succession of exceptionally organic-rich (>40% TOC) shales and carbonates interlayered with volcanic rocks and tuffs. At ~1.98 Ga old [2], it lies on carbonates which record the global Lomagundi δ¹³C_{carb} isotope excursion. It contains the earliest known occurrence of phosphorites and one of the oldest generations of oil.

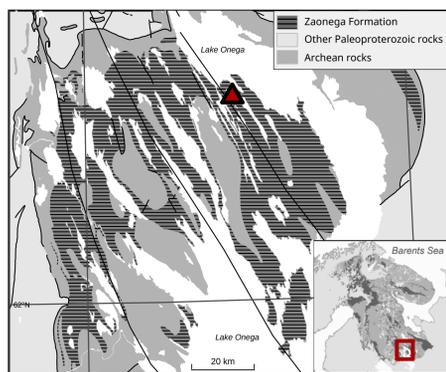


Figure 1: Location of the core sample site in the context of the Onega basin, NW-Russia.

Approximate total organic carbon (TOC) was calculated based on ashing at 500°C. Subsequent sample preparation was done in an ultraclean lab. Trace element concentrations of HF+HNO₃ digests were measured on a ThermoFisher Element2 HR-ICP-MS. Column chromatography was used to separate Mo from digested samples, after which isotopes were measured on a ThermoFisher NEPTUNE MC-ICP-MS using a ⁹⁷Mo–¹⁰⁰Mo double spike in a 1:1 ratio with natural Mo. δ^{98/95}Mo is reported relative to the standard NIST SRM 3134.

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Results

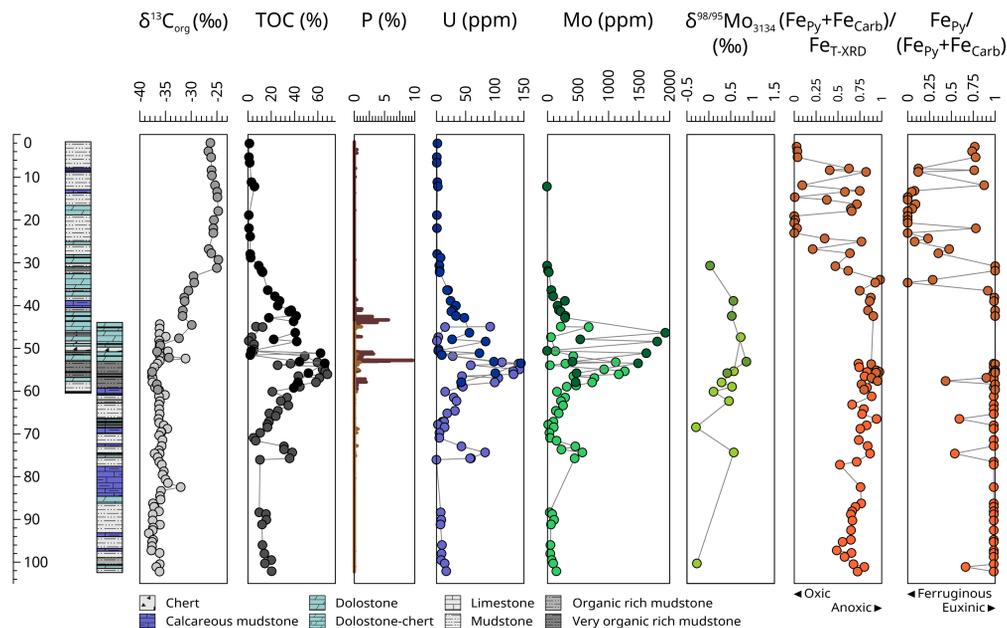


Figure 2: δ¹³C_{org}, total organic carbon (TOC), P, U and Mo concentrations, δ^{98/95}Mo and XRD-based Fe distribution in the studied section. δ¹³C_{org} and Fe distribution from [3]. A lithology-based correlation is used to combine chemostratigraphic data from the two cores into a continuous section.

Mo concentrations reach up to 2000 ppm in migrated pyrobitumen veins and more than 1000 ppm in finely-laminated, organic-rich mudstones in the middle of the section (Fig. 2). High enrichment is also evident in other redox-sensitive trace metals, such as U and V. The concentrations scale well with total organic carbon (Fig. 3).

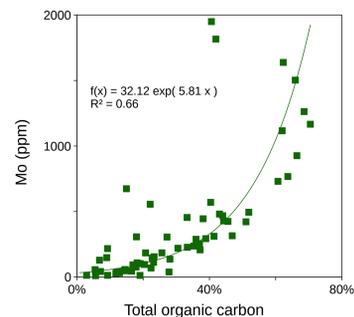


Figure 3: Mo concentration versus TOC.

δ^{98/95}Mo averages 0.42±0.81‰ and covaries with the Mo/TOC ratio (Fig 4). A peak in Mo concentrations and δ^{98/95}Mo in the middle of the

succession between 45 and 60 m coincides with a peak in other trace elements and TOC, as well as with a P-rich interval representing some of the world's first phosphorites.

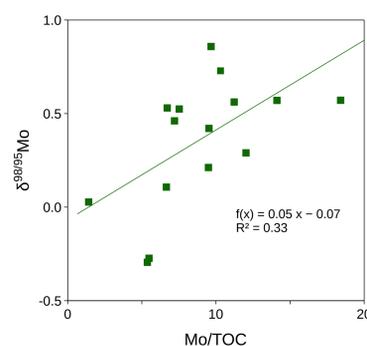


Figure 4: δ^{98/95}Mo versus Mo concentration normalized to TOC.

Organic matter in the lower part of the section has a distinctly methanotrophic signature (<-35‰ δ¹³C_{org}), but shifts to heavier (c. -25‰ δ¹³C_{org}), phototrophic values above the trace metal enrichment zone [4].

Implications

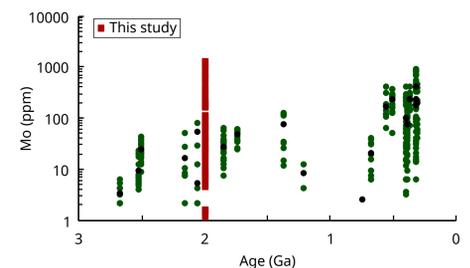


Figure 5: Secular trends in Mo concentrations in black shales. Modified from [1].

The measured Mo concentrations are the highest reported so far for Precambrian black shales (Fig. 5). Normalized to high TOC, however, samples from the ZF broadly overlap with previously reported values, but are up to two times higher (Fig. 6). The retention and concentration of Mo in migrated pyrobitumen veins suggests that the major part of Mo in the ZF is bound in organic phases, rather than sulfides.

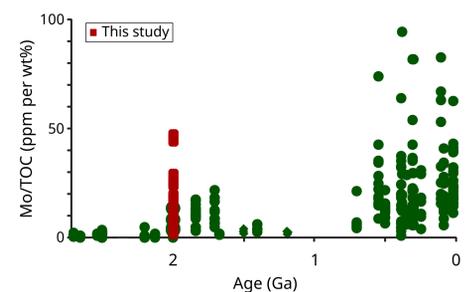


Figure 6: Secular trends in Mo concentrations in black shales, normalized to total organic carbon. Modified from [5].

An intriguing association of trace metal enrichment with methanotrophic δ¹³C_{org} signatures, as reported here, can also be seen in the 2.1 to 2.0 Ga Francevillian Basin [6].

Higher δ^{98/95}Mo values in the trace metal enrichment zone probably represent higher dissolved sulfide availability, leading to thiomolybdate formation and ultimately more efficient Mo drawdown with the organic fraction. Lower δ^{98/95}Mo in the upper and lower part correspond to fractionation in non-euxinic settings [7]. Our δ^{98/95}Mo values agree within error with those reported by Asael et al. [8], who found seawater δ^{98/95}Mo to be 0.46±0.21‰ during deposition of the upper ZF. Such low values suggest widespread anoxia in the depositional basin, which is recorded through several hundred meters of the ZF. However, since the studied section accumulated under a fluctuating redox environment where sulfidic conditions were constrained to porewater [3], our δ^{98/95}Mo values can only be taken as a minimum bound relative to seawater values.

Despite relatively widespread anoxia, the high Mo enrichment reported here still requires an undiminished Mo source through intensive oxic weathering of sulfides on the adjacent land mass. This scenario is hard to reconcile with a rapid collapse of the marine sulfate pool, that has been previously inferred from pyrite multiple sulfur isotope data in the upper ZF [9].

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