Geochemical Conditions During the Deposition of Tremadocian Alum Shale in the Baltic Paleobasin of Northern Estonia

Johannes Vind[a,b], Kaarel Mänd[b], Kalle Kirsimäe[b]

[a]Department of Mineral resources, Geological Survey of Estonia, Rakvere, Estonia, johannes.vind@egt.ee
[b]Department of Geology, University of Tartu, Tartu, Estonia, kaarel.mand@ut.ee, kalle.kirsimae@ut.ee

Alum Shale represents a widely recognised mudstone formation rich in organic content, spanning several hundred square kilometres across Scandinavia and the Baltic region (Nielsen & Schovsbo, 2011). This formation encapsulates over 20 million years of geological history, spanning the transition from the Cambrian to Ordovician periods, characterised by significant biotic events (Bian et al., 2023). In the eastern Baltic region, particularly within Estonian territory, the Alum Shale (locally referred to as graptolite argillite) is found as a younger and thinner succession. This 7-meter-thick sequence dates back to the Tremadocian age (Early Ordovician), with the earliest black shale interlayers originating from the Cambrian period (Stage 10). This study presents the analysis of samples from eight different drill cores, including their trace element compositions, and isotopic δ^{98}Mo and δ^{238}U data.

The trace element and isotope data have facilitated a better understanding of certain geochemical and basinal conditions during the deposition of Tremadocian Alum Shale in the eastern Baltic. Trace element proxies, focusing on uranium, molybdenum, vanadium, aluminium, and total organic carbon contents, suggest relatively open marine conditions. The pronounced enrichment of trace elements (Mo > 200 mg/kg, U > 100 mg/kg, and V > 1000 mg/kg) likely occurred within a perennial oxygen minimum zone on the shelf area rather than in a silled euxinic basin. Furthermore, Cd/Mo and Co×Mn cross-plots suggest the presence of upwelling in this geological system.

The determination of the combined δ^{98}Mo and δ^{238}U isotope system has provided insights into palaeoredox conditions. The δ^{238}U ratios exhibit a similar range of variability throughout the sections (-0.74 to -0.21‰, with an average of -0.44±0.14‰). In contrast, the δ^{98}Mo ratios categorise the samples into two distinct populations: a notably lighter δ^{98}Mo (−0.31 ± 0.14‰) at the Cambrian-Ordovician boundary and a heavier one (0.66 ± 0.21‰) in the Ordovician samples. In comparison to the older Miaolingian-Furongian Alum Shale (with δ^{98}Mo ~1.0‰ and δ^{238}U ~0.0‰; Zhao et al, 2023), both isotopes display lighter values in the currently examined sections. The coupled δ^{98}Mo and δ^{238}U system enables the modelling of the ranges of global coeval seawater composition (Lu et al, 2020). The possible δ^{238}U coeval seawater ratios during the Tremadocian period range from -0.89 to -0.34‰ (compared to modern seawater at -0.39‰). For δ^{98}Mo, the range extends from 0.7 to 1.67‰ (in contrast to modern seawater at 2.34‰). The lighter isotopic composition, compared to modern seawater and Miaolingian-Furongian Alum Shale, indicates the presence of relatively larger proportions of oxygen-deficient seafloor areas. Moreover, the combined geological record, spanning from the older Miaolingian-Furongian to the presently assessed Lower Ordovician Alum Shale, underscores notably dynamic and heterogeneous redox conditions during the deposition of Alum Shale in the Cambrian and Ordovician periods.

References

Bian, L., Chappaz, A., Schovsbo, N.H., Wang, X., Zhao, W., Sanei, H., 2023: A 20-million year reconstruction to decipher the enigmatic Cambrian extinction–Ordovician biodiversification transition. *Earth and Planetary Science Letters* 612, 118170.

Lu, X., Dahl, T. W., Zheng, W., Wang, S., & Kendall, B., 2020: Estimating ancient seawater isotope compositions and global ocean redox conditions by coupling the molybdenum and uranium isotope systems of euxinic organic-rich mudrocks. *Geochimica et Cosmochimica Acta*, *290*, 76-103.

Nielsen, A.T. & Schovsbo, N.H., 2011: The Lower Cambrian of Scandinavia: depositional environment, sequence stratigraphy and palaeogeography. *Earth Science Reviews* 107, 207–310.

Zhao, Z., Pang, X., Zou, C., Dickson, A. J., Basu, A., Guo, Z., ... & Dahl, T. W., 2023: Dynamic oceanic redox conditions across the late Cambrian SPICE event constrained by molybdenum and uranium isotopes. *Earth and Planetary Science Letters*, *604*, 118013.