Synchrotron-based constraints on the vanadium paleoredox proxy in the Tremadocian Alum Shale of Northeast Estonia, Baltic Paleobasin

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Reconstructing the redox conditions that prevailed in ancient oceans is vital to understanding the capabilities of the ocean to sustain life and will contribute to identifying the causes and implications of global biotic events such as the Cambrian explosion, the Great Ordovician Biodiversification Event and the Ordovician-Silurian Extinction. The traditional method to apply paleo-redox proxies mostly relied on examining concentration and, when possible, bulk isotopic signatures. Unfortunately, this can lead to multiple interpretations that makes constraining ancient redox conditions difficult. A novel approach to improve our interpretation of sedimentary records is to determine the speciation of redox-sensitive transition elements using synchrotron-based spectroscopy techniques.

Recent work has helped pioneer the determination of vanadium speciation—an emerging paleoredox proxy—in ancient rocks on the example of the late Cambrian Swedish Alum Shale [1]. Building on this, we used micro-focused synchrotron spectroscopy on samples across a W–E transect of the earliest Ordovician north Estonian equivalent of the Alum Shale (graptolite argillite) to (i) characterize the speciation of V using X-ray absorption fine structure (µ-XAFS) and to (ii) map sample-scale V distribution using X-ray fluorescence (µ-XRF).

Preliminary results confirm the prominence of V-sulfide species in ancient black shales, but obtained data highlight noticeable variability of V speciation. This confirms the representativeness of prior findings while underlining potential lateral heterogeneity and facies-dependence of V speciation in the extensive Baltic Paleobasin. Finally, we tie V speciation to independent transition-metal redox and hydrography proxies to provide firmer constraints on V cycling in sediments and its potential to record paleoredox.

[1] Bian et al. (2022) Geochim Cosmochim Acta, 338, 1-10.