

# The enrichment process of vanadium in Lower Ordovician vanadiferous black shales from Estonia: investigating critical metal resources in Europe

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Vanadium plays an important role in green technologies, such as energy storage. However, the accumulation pathways of vanadiferous black shales, one of the potential sources of vanadium, are not fully understood. To better interpret the V hyper-enrichment's origin, a high-resolution geochemical study was conducted on over 360 whole rock samples from 2 drill cores in the Lower Ordovician Türisalu Formation in northern Estonia (Baltic Palaeobasin). All samples were studied by X-ray fluorescence (XRF) and (CHNS) elemental analysis. Additionally, the fractionation of selected material was conducted with centrifugation, using both untreated and H<sub>2</sub>O<sub>2</sub>-treated black shale samples. The separated mineral fractions between <0.2 to >5µm and supernatant organic-rich fraction were studied using XRF and X-ray diffraction.

The results of the study revealed maximum V hyper-enrichment in the basal part of the Türisalu Formation, with V content reaching up to 2349 ppm and progressively decreasing towards the upper part of the formation. Distinctly, V distribution exhibited only moderate covariance with enriched Mo and U. The results of the fractionation experiment indicate that the main carriers of V are the finest mineral fractions (<2µm, mainly illite and illite-smectite), with V concentration up to 4832 ppm, while in organic-rich fraction V content remained rather low (200 ppm).

The observed very strong correlation between V, Cr, Al, and Ti further confirms that the mechanism of hyper-enrichment of V in black shales was largely controlled by clay minerals and associated with dissolved organic matter (DOM) [1], [2]. Reduction of V in the non-sulfidic water column, its complexation with organic ligands, and the sorption of such complexes to clay particles is suggested as a major pathway for V capture in the studied setting. Clay-bound V might have transported to sediment via flocs of clay particles and DOM.

[1] L. Bian *et al.*, (2021), *Int. J. Coal Geol.* 239.

[2] GN Breit et RB Wanty, (1991), *Chem. Géol* 91, 83–97.

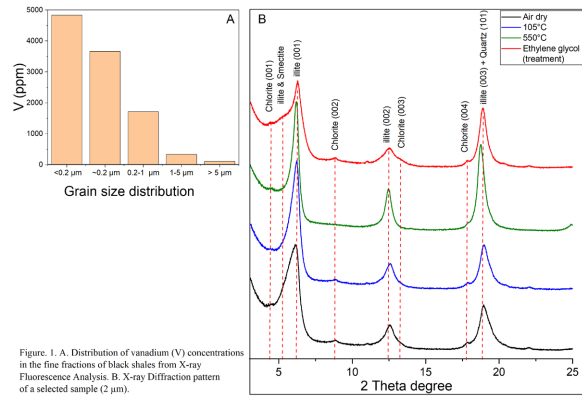


Figure 1. A. Distribution of vanadium (V) concentrations in the fine fractions of black shales from X-ray Fluorescence Analysis. B. X-ray Diffraction pattern of a selected sample (2 µm).

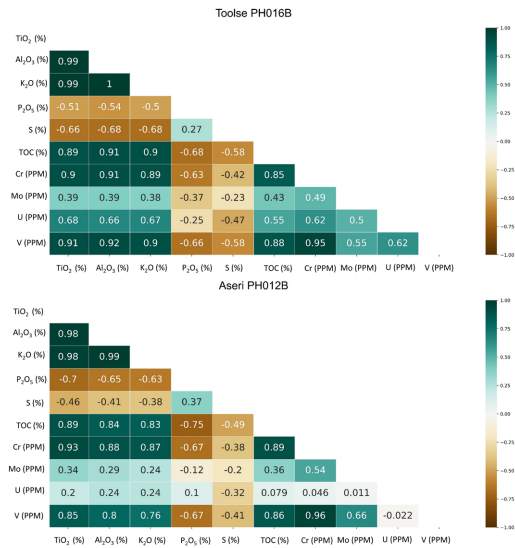


Figure 2. The correlation matrices with Pearson correlation coefficients for analysed V-rich black shale samples from the Toolse PH016B (n=110) and the Aseri PH012B drill cores (n=94).