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# Multi-Analytical Investigation of Oil Shale and Its Ash Fractions: Trace Element Partitioning and Environmental Implications

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## Abstract

This study presents a comprehensive multi-analytical investigation of oil shale and its combustion ash fractions using XRD, XRF, and LA-ICP-MS techniques. The mineralogical composition is characterized by a transition from carbonate-rich phases in raw shale to silicate-dominated assemblages in ash, accompanied by systematic changes in major oxides. Trace elements such as Cr, Pb, As, Ni, and Cd exhibit distinct partitioning patterns across WHB, Cyclone, and ESP ash fractions, with WHB ash showing the highest enrichment for most elements. Matrix-matched calibration ensures reliable quantification of trace elements. The results highlight the role of mineral transformation and ash morphology in governing element mobility during combustion. Notably, potentially hazardous elements tend to accumulate in coarse ash fractions, raising environmental concerns regarding ash disposal and reuse. These findings provide valuable insights into the geochemical behavior of trace elements during oil shale combustion and offer guidance for environmental risk assessment and waste management strategies.

**Keywords:** Oil shale, Ash, Mineralogical composition, Chemical composition, Trace elements

## 1. Introduction

As a major unconventional hydrocarbon resource, oil shale contributes significantly to the energy mix in regions such as Estonia, where it remains a strategic domestic energy source. However, the thermal utilization of oil shale generates substantial amounts of ash, which may contain elevated concentrations of potentially hazardous elements (PHEs) such as Cr, Pb, As, and Ni (Raj *et al.*, 2022). The environmental behavior of these elements is closely linked to their chemical forms and mineral associations, which can be profoundly altered during combustion (Vejahati *et al.*, 2010). Despite growing attention to oil shale combustion byproducts, previous studies have typically focused on either bulk chemical composition or mineralogical features in isolation, limiting our understanding of the integrated geochemical transformation processes that govern trace element behavior.

To address this gap, the present study conducts a multi-analytical investigation of oil shale and its combustion ash fractions, namely waste heat boiler (WHB), Cyclone, and electrostatic precipitator (ESP) ash, using X-ray diffraction (XRD), X-ray fluorescence (XRF), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). These methods enable detailed characterization of mineral assemblages, major oxides, minor and trace elements, respectively. Special attention is given to the enrichment patterns of trace metals across ash fractions and their environmental implications. By linking mineralogical transformations to element mobility, the study provides insights into pollution control, waste valorization, and the sustainable management of oil shale combustion residues.

## 2. Materials and Methods

### *2.1. Sample preparation and compositional analysis*

Representative samples of raw oil shale, semicoke, and ash from the power plant were collected and dried, ground, and homogenized. XRD analysis was conducted to identify and quantify major mineral phases. XRF analysis was used to determine the bulk oxide composition, providing an essential basis for matrix characterization and correction. Samples and selected standards are fused in LiB glass separately for further analysis.

### *2.2. Matrix matching and trace element quantification*

To improve the accuracy and precision of trace element quantification, a KNN algorithm was employed to select chemically and mineralogically similar CRMs/SRMs for matrix-matched calibration in both LA-ICP-MS and solution-based ICP-MS analyses. For LA-ICP-MS, the

NIST SRM 610 was used for initial instrument tuning. Fine-tuning was then conducted based on the selected optimal CRM/SRM, using response surface methodology and experimental validation. A hybrid calibration strategy was applied using the selected CRM/SRM as the external standard and XRF-derived concentrations as internal references for minor and trace element quantification.

## 3. Preliminary Results and Discussion

The mineralogical and chemical compositions of oil shale and its ash fractions vary significantly. From raw shale to the high-ash ESP fraction, carbonate minerals, mainly calcite, and their CaO and MgO contents decrease, while siliceous minerals (quartz), potassium feldspar (adularia), and aluminosilicates like muscovite increase, with corresponding rises in $SiO_2$ and $Al_2O_3$, indicating silicate dominance. $SO_3$ and $K_2O$ fluctuate across fractions, showing mineralogical complexity. Chlorite (a hydrous mineral) and sylvite (KCl, a salt mineral) appear only in the ESP fraction. $Fe_2O_3$ remains relatively stable, while $TiO_2$ increases in higher ash fractions, suggesting enrichment of heavy mineral fraction. Overall, oxide trends support a shift from carbonate-rich to silicate- and secondary mineral-rich assemblages. Corresponding to these mineralogical and chemical changes, combustion also significantly alters the distribution of trace and minor elements in oil shale, with the WHB ash exhibiting the most pronounced enrichment. Elements such as V, Cr, Ni, Cu, Zn, Ba, and Pb are highly concentrated in WHB ash, indicating substantial migration and incorporation during the initial stage of ash formation. As also shows its highest concentration in WHB ash, likely as a result of volatilization followed by redeposition (Xu, 2004). In contrast, Mn is slightly more enriched in Cyclone ash, possibly due to differences in mineral carriers or separation dynamics. Although Ba and Pb are elevated across all ash types, their concentrations peak in the WHB ash. Additionally, radioactive elements Th and U are notably enriched in both WHB and ESP ash fractions, suggesting incomplete volatilization (Yu *et al.*, 2005) and raising concerns about their potential environmental impacts. Overall, the combustion process promotes the accumulation of multiple hazardous and potentially toxic elements in ash residues, particularly within the WHB fraction. This highlights the need for further research into their environmental behavior, mobility, and the implications for waste management and resource recovery.

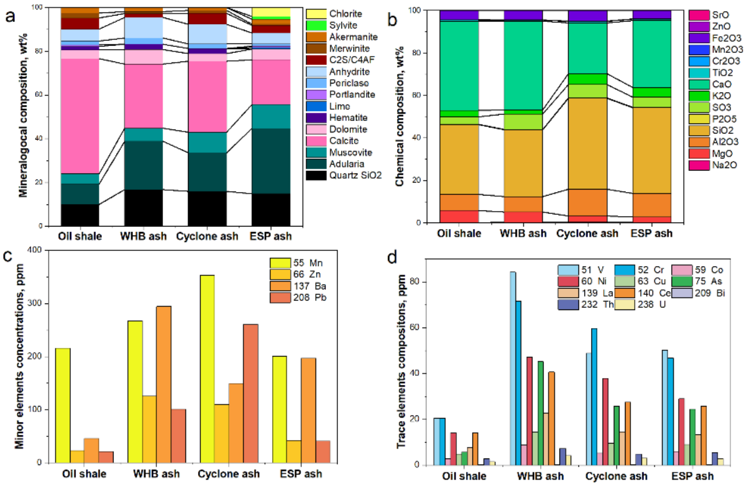

**Figure 1.** Mineralogical, chemical, and elemental composition of oil shale and its ash fractions. (XRD data (in Figure 1(a)) is adapted from Ummik et al., 2025, with Open Access under the license of CC BY 4.0.)

## 4. Conclusion

This study demonstrates that a multi-analytical approach effectively reveals the mineralogical and chemical transformations of oil shale during combustion, as well as the partitioning behavior of trace elements. The observed element partitioning highlights potential environmental risks associated with ash residues. These findings underscore the necessity for comprehensive investigations into the environmental behavior and mobility of trace elements to inform effective waste management and resource recovery strategies.

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