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Statistical Analysis of Microelement Trends in Graptolitic Argillite, Northern Estonia

O.P. Nzekwe* (INRS-ETE), R. Lehné (Technische Universität Darmstadt) & O. Lenz (Technische Universität Darmstadt)

SUMMARY

This work presents a statistical analysis of microelement trends in graptolitic argillite (oil shale variety) in northern Estonia with respect to the spatial extent and compositional dynamics of the shale layers. Graptolite argillite is characterized by significant amounts of microelements (U, Mo, Zn, etc.). Statistical analysis namely, correlation analysis, principal component analysis (PCA) and canonical correspondence analysis (CCA) indicates other prevailing trends. PCA suggests microelements associations while CCA shows the relationship between microelements and “environmental” factors. These trends possibly indicate variable composition of organic matter/mineral particles in graptolitic argillite in northern Estonia.
Introduction

The Late Cambrian to Ordovician crustal section in Estonia contains kukersite oil shale as well as graptolite argillite (*Dictyonema* shale). Kukersite has been mainly mined due to its higher calorific value (9–11 MJ/kg). On the other hand, graptolite argillite has a lower calorific value (4.2–6.7 MJ/kg); consequently it has not been mined as a source of fuel (Kattai & Puura, 1988; Raukas & Teedumäe, 1997). However, graptolite argillite is characterized by significant amounts of microelements including U, Mo, Zn, Pb and other metals; thus can be treated as a potential source of metal ore and/or two-fold energy including U and shale oil (Raukas and Punning, 2009). In order to evaluate the microelement potential in graptolitic argillite, spatial and statistical analyses are necessary (Valgma, 2003). A relatively easy pancake geology which can be induced from a geologic map of Estonia (Kalberg *et al.*, 2007) suggests a more or less even pattern of resource distribution but spatial analysis of well data (520 wells) using geographic information systems (ArcGIS) showed that relatively high contents of microelements: U (>200 ppm), Pb (> 200 ppm), Mo (> 300 ppm), Zn (> 200 ppm), V (> 1000 ppm), Th (> 11 ppm) and Ag (> 0.7 ppm) occur in northeastern Estonia. Furthermore, a statistical analysis of the well data was performed to better understand trends between microelement concentration, the depth of upper surface of graptolitic argillite, and calorific value.

Methods

PAleontological STatistic (PAST) software version 2.12 (Hammer *et al.*, 2001) was used to analyse data from 520 wells in northern Estonia. Well data included: X, Y, Z coordinates of wells; depth of upper and lower surfaces of graptolitic argillite; thickness of argillite units; concentration of microelements Uranium (U), Lead (Pb), Molybdenum (Mo), Zinc (Zn), Vanadium (V), Thorium (Th) and Silver (Ag), as well as calorific value for some layers. The principles of analysis applied were univariate analysis, correlation analysis, principal component analysis and canonical correspondence analysis. Univariate analysis involved calculating measures of location (mean, median and mode); measures of spread (variance, standard deviation, interquartile ranges) and measures of shapes (skewness and kurtosis) for microelement concentrations. Correlation analysis involved the study of the linear association between two variables (e.g. concentration vs. depth). The principal component analysis (PCA) is a classical statistical method which transforms a multivariate set of possibly correlated variables into groups of uncorrelated variables called principal components using the eigenvector-eigenvalue based statistical approach (Enikanselu & Ojo, 2012). The analysis attempts to deduce similarities/difference in microelement associations (Fig. 1). Canonical correspondence analysis (CCA) is a correspondence analysis of a site/species matrix where each site has given values for one/more environmental variables (Legendre & Legendre, 1998). For this study, calorific value and depth of upper surface of graptolitic argillite were considered as environmental factors (Fig. 2).

![Figure 1](image-url)  
*Figure 1* Principal component analysis (PCA) scatter diagram showing associations (groups) among microelements in graptolitic argillite (black dots indicate sample number).
Figure 2 Canonical correspondence analysis showing trend of microelement concentrations with respect to some environmental factors (calorific value and depth of upper argillite surface); black dots indicate sample number.

Conclusion
The spatial distribution map of microelements in graptolitic argillite shows that northeastern Estonia is characterized by distinctly high concentrations of U, Pb, V, Mo and Ag relative to other areas. Statistical analysis of available well data revealed more prevailing patterns. Spearman’s rank-order correlation test suggests weak to no monotonic association (p > 0.05) between microelement contents and depth of upper surface of graptolitic argillite, as well as calorific value. Principal component analysis (PCA) shows that the microelements can be grouped into 3 associations comprising (1) U, Mo and V; (2) Pb and Ag; and (3) Zn and Th (Fig. 1). Canonical correspondence analysis suggests a clear association of calorific value with Zn and Pb contents; and also between V contents and depth of upper surface of graptolitic argillite (Fig. 2). These trends possibly indicate variable composition and content of organic matter or mineral particles in graptolitic argillite.

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