

<https://doi.org/10.3176/oil.1995.3.06>

MICROELEMENTS IN ESTONIAN AND GREEN RIVER (U. S. A.) OIL SHALES: A QUANTITATIVE COMPARISON

L. PETS

Tallinn Technical University
Tallinn, Estonia

Ü. HALDNA

Estonian Academy of Sciences
Institute of Chemistry
Tallinn, Estonia

Estonian and Green River (U.S.A.) oil shales as well as their ashes were compared on the basis of the content of 38 elements, measured by neutron activation analysis.

Due to the deficiency and high price of crude oil and gas in all countries, more and more attention is shifted to the use of local fuels. As a rule, the local fuel is less energy-rich and needs special technology for utilizing, including rather expensive devices for cleaning the flue gases. In some countries, including the U.S.A. and Estonia, oil shale belongs to the local fuels.

The Estonian oil shale deposits form a part of the Baltic oil shale basin, and are located in the western part of this basin. According to the origin of these oil shales, kukersites are related to the fuels formed in the ancient sea. The kukersites are of medium age. They were formed in a weakly acidic geochemical environment. The original material of kerogen is still a matter for discussion: according to some authors it is a kind of blue-green algae, but the allogenic origin is also not ruled out [1]. In Estonia, three uses have been developed for oil shale. One of them is its direct burning for producing electrical energy. The building of two power plants burning oil shale has made oil shale a notable part of the energy balance of the Country [2]. According to official data, oil shale energy makes up a considerable part of the energy balance of Estonia: in 1993 about 16.5 million tons of oil shale were burned for producing electricity, and that constitutes about 65 % of the total fuel energy used in that year. This was about 4% more than the previous year, 1992 [3].

The most important part of the U.S.A. resources of oil shales are related to the so-called Eocene formation of shales in the Green River Formation. These oil shales are found in seven basins located in three

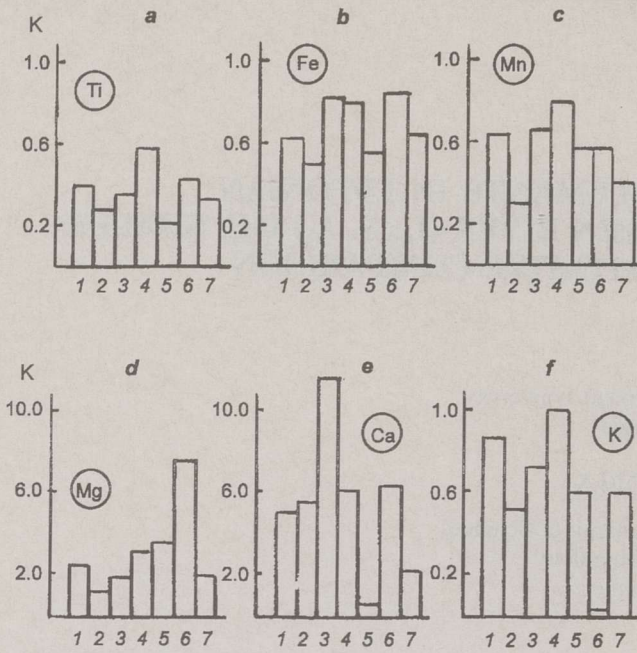


Fig. 1. Enrichment/impoverishment factors of the macroelements (a) Ti, (b) Fe, (c) Mn, (d) Mg, (e) Ca, and (f) K

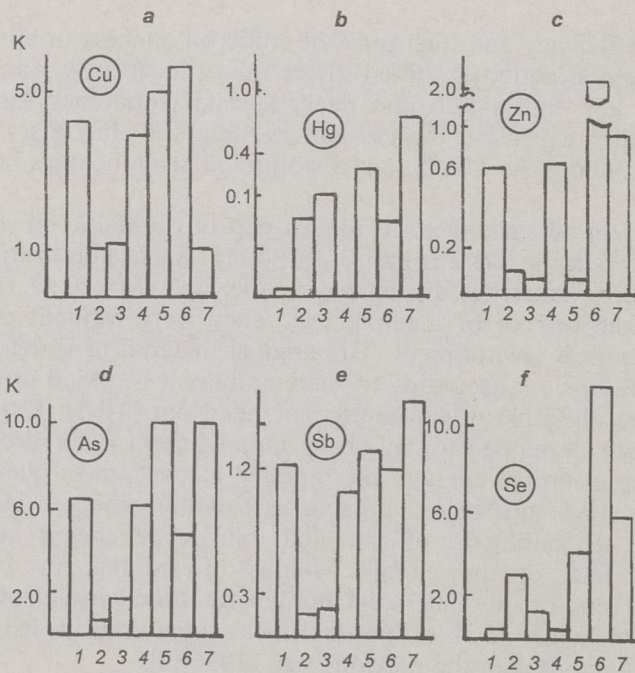


Fig. 2. Enrichment/impoverishment factors of the chalcophilic microelements (a) Cu, (b) Hg, (c) Zn, (d) As, (e) Sb, and (f) Se

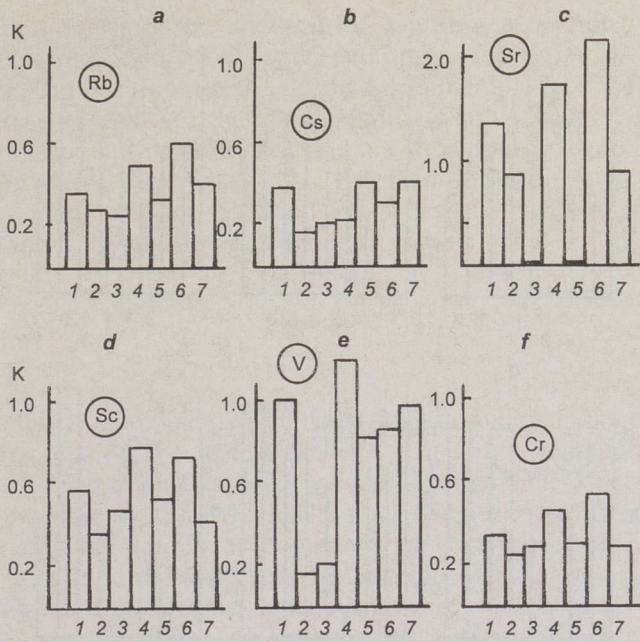


Fig. 3. Enrichment/impoverishment factors of the lithophilic microelements (a) Rb, (b) Cs, (c) Sr, (d) Sc, (e) V, and (f) Cr

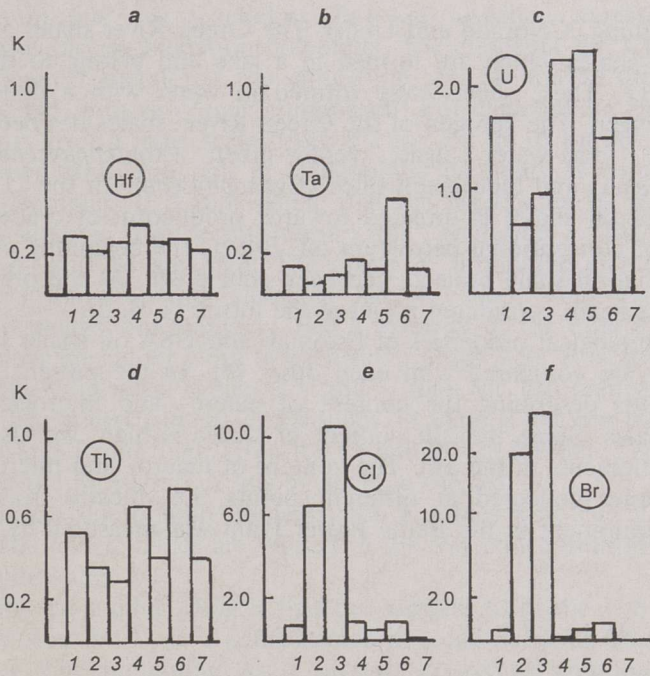


Fig. 4. Enrichment/impoverishment factors of the lithophilic microelements (a) Hf, (b) Ta, (c) U, (d) Th, (e) Cl, and (f) Br

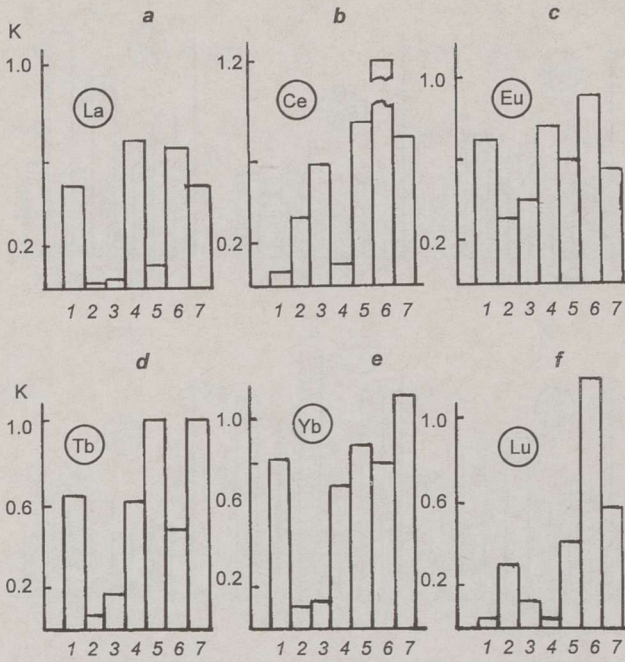


Fig. 5. Enrichment/impoverishment factors of the lithophilic microelements (a) La, (b) Ce, (c) Eu, (d) Tb, (e) Yb, and (f) Lu

states (Wyoming, Colorado and Utah). The Green River shales are similar to orogenic shales which are formed in a lake and belong to the Paleogene-Neogene age. These shales were formed in water with a deficiency of dissolved oxygen. The kerogen of the Green River shales has been formed from three fresh-water algae: yellow-green (*Xanthophyceae*), green (*Chlorophyceae*) and blue-green ones (*Cyanophyceae*). In the U.S.A., the utilization of oil shales is directed towards production of crude oil as a substitute for conventional petroleum oil. But by the beginning of 1982 all the substantial oil shale projects had been shut down. At the present time oil shales are again considered a fuel of the future [1, 4, 5].

The technological properties of Estonian and USA oil shales have been studied and are compared with each other [6]. In the present paper we present results describing the content of macro- and microelements of these oil shales. Since the ash content of shales is high, we also present data about elements in the ash. The content of macro- and microelements in ash samples collected at different points, i.e. mostly from fly ash collecting equipment in the Baltic Power Plant was measured by us earlier [7-11].

Methods

The samples of shales were ashed in laboratory electrical furnaces. The shale samples were analysed for eight macroelements and for 30

microelements using the method of neutron activation analysis. The enrichment coefficients (K) were determined in order to compare the elemental composition of the studied samples. These coefficients were calculated with regard to the corresponding Clark values of these elements as found in the earth's core [12], and are shown as histograms in Figs 1-5: 1 - Green River Basin shale, 2 - Estonian shale; shale ashes from: 3 - Estonia, 4 - Uinta Basin, 5 - Sand-Wash Basin, 6 - Piceance Creek Basin, and 7 - Green River shale (calculated from data given in [15]).

Discussion

The enrichment coefficients calculated for the macroelements are given in Fig. 1. For Ti, Al, Fe and Mn the K values are somewhat lower than compared to the respective Clark values. A remarkable aspect is that these K values are rather close to each other. The Green River samples are relatively rich in sodium as compared to the respective Estonian shale samples. All the samples studied contain a lot of calcium and magnesium. The maximum calcium enrichment occurs in the ash of Estonian shale ($K = 11.7$) and the maximum enrichment for magnesium occurs in the ash of shales from Piceance Creek Basin ($K = 7.6$). The microelements are divided into the groups widely used in geochemistry (i.e. chalcophilic, lithophilic and siderophilic). For eight chalcophilic elements (Zn, Cu, Hg, Ag, Au, As, Sb, Se) the K values were calculated (Fig. 2). The first five elements in this row (excluding Zn) are so-called transition elements which have varying oxidation potentials. The elements Zn, Cu and Hg are typical "heavy" metals. At the same time, As, Sb and Se are nonmetallic elements and form very toxic compounds. For chalcophilic elements the K values vary over a large scale: from 0.2 for Hg to 10 for As. The samples from Green River are rich in chalcophilic elements as compared to the Estonian samples. It is remarkable that the Hg content is very low in all analysed samples. The second remarkable conclusion is that the K values for Cu, As and Se are high. The group of lithophilic elements is rather large (21) and contains elements like K, Na,... and Ca, Ba,..., the transition metals and halogens. For a majority of the lithophilic elements the K values are rather close to each other (Figs 3-5). It is notable that the Green River shales are richer in V and U than the Estonian shales (Figs 3e and 4c). The metal content in Estonian oil shale is low but the coefficients K for Cl and Br are high (10.4 for Cl and 20-25 for Br). This is probably related to the formation of this oil shale in the sea.

As for the siderophilic elements, the K values were calculated only for cobalt. The low K values are related to the low concentrations of cobalt in the samples studied.

A truly remarkable thing is that the samples from the U.S.A. contain a lot of As ($K = 5-10$). It is concentrated in some minerals (skutterudite and safflorite). The remaining As is present in oxygen compounds. The oil from Green River oil shales contains about 3-4 % As [13]. If this shale is burned, a large part of As remains in ash [13]. The ecological behaviour of

As is as follows: it has a medium or low mobility in the environment and does not concentrate much in soil, air, water and biogenic material [14].

Conclusions

Using the method of neutron activation analysis, 38 elements were measured in Green River and Estonian oil shale samples, including some ashes of these shales. The analysis of these data is based on a comparison of the enrichment coefficients for the respective elements against the Clark values. The low metal content of oil shales has once again been established. The American oil shale and its products are often rich in various metallic and nonmetallic elements. The Estonian oil shale and its products are remarkably rich in Cl and Br, reflecting the formation of this shale in the sea.

Acknowledgment

The authors are grateful to American colleagues for their help in collecting the data.

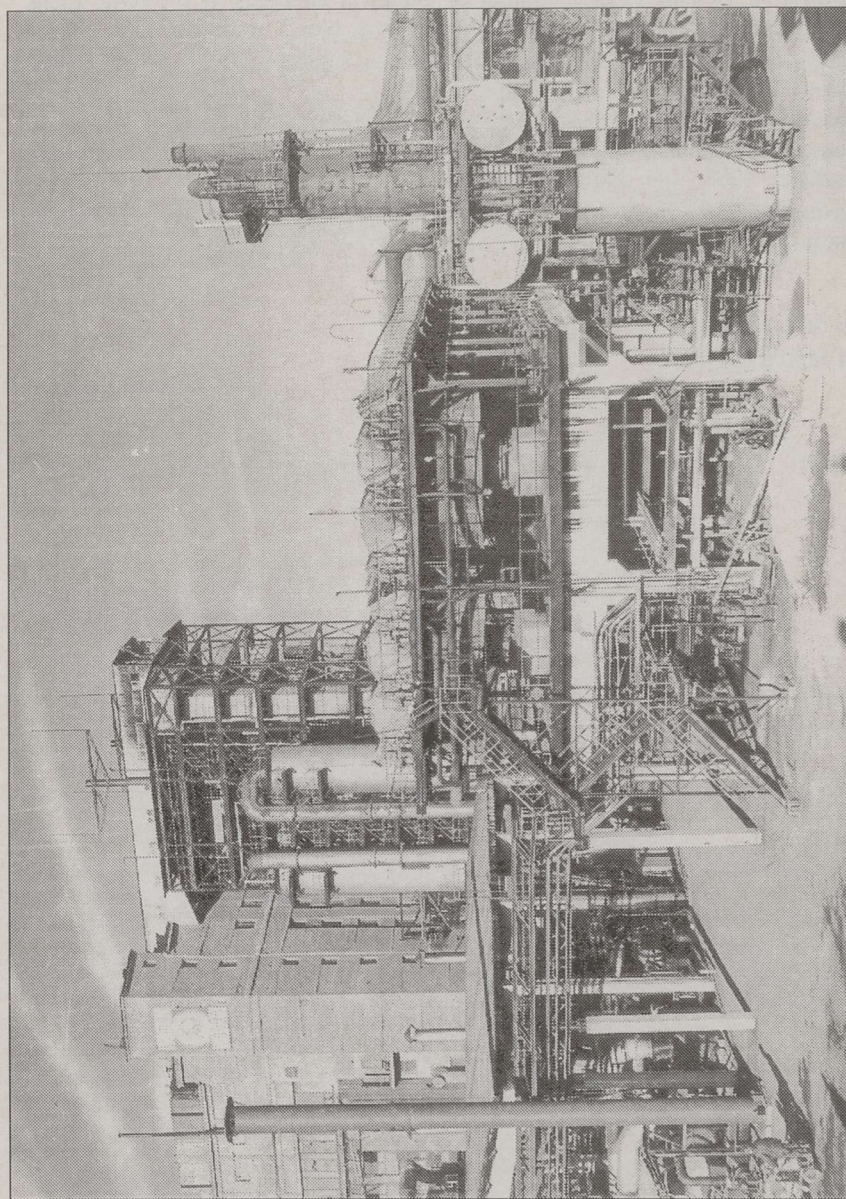
REFERENCES

1. Oil shale deposits (ed. V. F. Tcherepovski). - Moscow, 1988 [in Russian].
2. *Aarna A., Öpik I.* Utilization of oil shale in the Estonian SSR [in Russian, with English summary] // Oil Shale. 1984. V. 1, No. 1. P. 7-15.
3. Fuel Consumption and Waste Products : Statistical bulletin. - Tallinn, 1994 (in Estonian).
4. *Öpik I.* About the perspectives to utilize oil shale and bituminous sand [in Russian, with English summary] // Oil Shale. 1984. V. 1, No. 1. P. 104-108.
5. *Turner I. P., Rothwell R. A.* Geotechnical properties of combusted western oil shale // Environm. Geol. Sci. 1991. V. 17, No. 3. P. 249-257.
6. *Yefimov V. M., Kundel H. A.* Retorting properties of Green River and Irati oil shales [in Russian, with English summary] // Oil Shale. 1989. V. 6, No. 1. P. 37-43.
7. *Pets L. I., Vaganov P. A., Knoth Y. et al.* Microelements in oil-shale ash of the Baltic Thermoelectric Power Plant [in Russian, with English summary] // Oil Shale. 1985. V. 2, No. 4. P. 379-390.
8. *Pets L. I., Vaganov P. A., Schnier C.* Lanthanides in the oil shale ash of the Baltic Thermoelectric Power Plant [in Russian, with English summary] // Oil Shale. 1986. V. 3, No. 4. P. 419-425.
9. *Pets L. I., Miller A. D.* Rhenium in the oil shale ash of the Baltic Thermoelectric Power Plant [in Russian, with English summary] // Transactions Tallinn Polytech. Inst. 1989. No. 685. P. 93-96.

10. *Pets L. I., Ott R. E.* Mercury in oil shale mineral matter [in Russian, with English summary] // Oil Shale. 1989. V. 6, No. 3. P.289-290.
11. *Pets L. I., Grosse J. I.* Florine in mineral matter of Estonian oil shale combustion products [in Russian, with English summary] // Oil Shale. 1993. V. 10, No. 2-3. P. 211-219.
12. *Vinogradov A. P.* The average content of chemical elements in the basic rocks of earth's crust [in Russian] // Geokhimiya. 1962. No. 7. P. 555-571.
13. Standard and Reference Materials for Marine Science. Green River Shale. Unesco. - 1993. No.25. P. 277-278.
14. *Jaganathan J., Mohan M. S., Zinaro R. A., Irgolic K. J.* Speciation of arsenic in a Green River oil shale and shale retort waters // J. of Trace and Microprobe Technology. 1985. V. 3, No. 4. P. 345-375.
15. *Gamayurova V. S.* The Arsenic in Ecology and Biology. - Moscow, 1993 (in Russian).

Presented by I. Öpik

Received January 3, 1995



Retorting station GGS-6 at RAS "Kiviter" in Kohtla-Järve