ESTONIAN GRAPTOLITIC ARGILLITES – ANCIENT ORES OR FUTURE FUELS?

E. LIPPMAA[*], E. MAREMÄE, A.-T. PIHLAK, R. AGURAIUJA

National Institute of Chemical Physics and Biophysics
Akadeemia tee 23, 12618 Tallinn, Estonia

The Estonian black argillites formed in Late Cambrian and Early Ordovician (Tremadoc) just after the Cambrian evolutionary explosion, nicely illustrated by the famous Burgess shales. The abundant new Cambrian lifeforms were well able to thrive in anoxic poisonous and strongly radioactive waters, rich in U235. They belong to the extensive formation of the Cambrian-Ordovician black shales which form patches in the latitudinal zone extending from Lake Ladoga in the east to the Jutland Peninsula in the west. In the black mudstones at Sillamäe the most enriched elements are, in the order of biocapture efficiency, molybdenum, carbon, rhenium, antimony, uranium and arsenic. It appears that not only the most unusual chemical composition, but also the very large compositional variability might depend upon even faraway metamorphic processes and long-transported allochtons during the Finnmarkian and Caledonian orogenies. The Sillamäe black shale is certainly a better metalliferous ore than the comparable product from Jämtland, Sweden. It is also a very good future fuel, but only nuclear. The carbon content is too low for anything except providing process heat for production of rare metals.

Introduction

The Estonian black argillites and mudstones were formed during the period of time from Late Cambrian (Furongian) to Early Ordovician (Tremadoc). The Cambrian black shales were severely denuded, reshuffled and redeposited over a large area, but those formed in Tremadoc during the Pakerort and Varangu (formerly Ceratopyge) regional stages have largely remained as the constitutionally very different Eastern and Western facies of the same (?) part of the Türisalu formation. The brown kukersite shale was deposited in Late Ordovician at 461 to 459 Ma. All the shale-related events thus took place over a significant timespan from about 500 Ma to 460 Ma, or just up to the Kukruse stage in Regional Standard. The North Estonian Klint shows all

---

[*] Corresponding author: e-mail *elippmaa@nicpb.ee*

these series, stages and formations from Kukruse (on some islands only) down to the massive blue clay of Lontova [1–3]. This clay with a sedimentation age of 530 Ma is constitutionally much older with a Rb/Sr age of 860 Ma or Sm/Nd date 790±90 Ma and stems from metamorphic rocks with an age close to 900 Ma, formed during the Sveconorvegian Orogeny which was the major sediment source in Baltoscandia during the Late Vendian and Early Cambrian [4]. Massive amounts of allochtonous orogenic material can thus travel a long way. This circumstance must be seriously considered in connection with the later Caledonian Orogeny which was a long mountain-building process that stretched from Tremadoc to Early Devonian [2, 5]. Large amounts of rare heavy elements were then incorporated into black alum shales and mudstones in Norway, Sweden, Denmark and Estonia. There are no local autochtonous sources for these elements in the Baltic area. The only known origin is the squeezed Iapetus ocean.

The chemical composition of Estonian argillites

Estonian argillites have for a long time been known as Dictyonema shale [1], and the appearance of the first planktic graptolite *Dictyonema flabelliforme* (now *Rhabdinopora flabelliformis*) was taken as the local base of the Ordovician system. More lately conodonts are used as parallel fossil markers. The Global Stratotype Section and Point (GSSP) for the base of the Ordovician is currently nailed down in Newfoundland with *Iapetognathus fluctivagus*, just (hopefully) below the earliest graptolites.

Actually the Baltoscandian argillites are chemically not homogeneous and uniform. Even quite closely spaced locations in the same facies can contain chemically quite different argillite material. A good example is provided by the central (Maardu O_1trT west) part of the Türisalu formation, the Eastern (Sillamäe O_1trT east) part of the same facies and an interesting mixed stretch (Orasoja O_1trO) close to the Narva River [6, Fig. 2.]. Surprising differences can be found in the distributions of abundances and enrichment factors of both the chemical elements and oil yields, particularly in a juxtaposition of the argillites from Sillamäe and Maardu [7].

The oil yields were determined in the Franz Fischer aluminum retort under standard conditions, heating it to 530 °C. The abundances of the main elements were determined by X-ray fluorescence (XRF) spectroscopy on a S4 Explorer Spectra plus Bruker analyzer [8]. Pressed pellets were used and the analysis was facilitated by the extremely small particle size of the metalliferous organic matter. Organic matter content and elemental analysis were carried out with standardized chemical methods, see Tables 1 and 2.

The Sillamäe black shale sample is taken from the mine formerly used for uranium production from 1948 to 1952 [9]. The Maardu argillite sample is from the former phosphorite open cast quarry in Maardu [10].

Table 1. **Content of the ubiquitous elements in the argillite samples (in %)**

Element	Abundance % as oxide/element		Abundance in Earth crust as element, % [11]
	Sillamäe	Maardu	
SiO_2	38.11	45.30	28.2
Al_2O_3	9.10	12.26	8.23
CaO	10.98	0.23	4.15
Fe_2O_3	6.92	4.02	5.63
K_2O	5.73	8.36	2.09
S	3.18	1.84	0.035
MgO	1.32	0.80	2.33
P_2O_5	0.57	0.05	0.11
TiO_2	0.53	0.78	0.57
ZnO	0.35	0.01	0.01
MnO	0.14	0.01	0.10
Na_2O	0.06	0.06	2.36
Cl	0.02	0.02	0.02
C	12.1	11.9	0.02
Sum*	89.1	85.6	

*The difference between total sum and table sum is caused by the non-carbon components of the organic matter and moisture.

Table 2. **Abundance of rare elements in the argillite samples (in mg/kg = ppm)**

Element	Abundance as element, in ppm [8]		Abundance in Earth crust as element, in ppm [11]	Relative enrichment at Sillamäe
	Sillamäe	Maardu		
As	120	33	1.8	**67**
Ba	345	410	425	–
Cd	5	0.2	0.15	33*
Ce	79	17	66.5	–
Cu	200	48	60	–
Ga	7	17	19	–
La	33	10	39	–
Mo	980	82	1.2	**817**
Nb	7	14	20	–
Ni	152	40	84	–
Pb	180	158	14	13
Rb	88	130	90	–
Re	0.134**	0.08	0.0007	**191***
Sb	37	6.4	0.2	**185***
Sc	0	10	22	–
Se	2.5	0	0.05	**50**
Sr	59	64	370	–
Th	0	0	9.6	–
U	257	31	2.7	**95**
V	901	498	120	7.5
W	0	0	1.25	–
Y	45	3	33	–
Zn	3476	84	70	**50**
Zr	129	143	165	–
C	121 000	119 000	200	600

*   The data of V. Petersell
** Toolse [10]

It is immediately clear that extreme selectivity of enrichment favoring Mo, U, Sb, As and Zn, even Re, does not correlate with adsorption on clays. It appears rather to depend upon the biological preferences of some ancient organism living under most unusual anoxic, poisonous and highly radio-active conditions. Such environment would kill off most of the present fauna, but it may have been very advantageous for explosively fast creation of unimaginable new species not by evolution, but by the radioactive dice-casting shortcut. It is also important to note that enrichment of molybdenum has been more efficient than that of carbon. Argillites can therefore be more like metalliferous ores than a form of real fossil fuel.

Comparison of the Sillamäe argillite with the other close to zero oil yield black shale from Jämtland (26 billion tons) provides striking similarities [10, 12–14], see Table 3.

Table 3. **Comparison of argillites**

Deposit	Oil yield, %	Abundance of elements, g/ton					
		Mo	V	U	Ni	Zn	Re
Sillamäe	<0.2	980	901	257	152	3475	
Jämtland	0	238–313	1510–1870	170–185	300–405	410–430	
Toolse	0.8	406	1040	162	300	1500	0.134
Maardu	2.6	81	498	31	40	84	0.080

The caledonides connection

The history of maturation of Estonian argillites begins in the Proterozoic era when the Jotnian sedimentation was followed by massive denudation with the formation of the sub-Cambrian peneplain and the first arenaceous and argillaceous sediments on it. The Paleozoic sea transgression connected the Baltic syneclise with the Moscow basin and the ancient oceans. These links introduced the Early Cambrian trilobites into the Baltic sea and Fenno-scandia [3]. By the end of the Lontava stage, the Baltic area was inundated again. Even the latest black shales formed in the Early Tremadoc were partially washed away, particularly in the Eastern facies [1, 14].

Black alum shales formation in Late Cambrian and Tremadoc was a parallel development to a much more grandiose mountain building during the Scandinavian Caledonides with numerous tectonic deformation events between 540 and 400 Ma in a broadest sense [2, 5, 15, 16]. The enigmatic Finnmarkian event in the North of Norway at about 489 Ma, whether a true orogeny, an arc-continent collision followed by subduction, or just a trans-tensional mega-shear zone certainly provided metamorphic shale material heated between 150 and 550 °C and sideways thrust for lithological facies folding and for spreading the allochtons as far as Oslo. The first event was followed by continuous orogenic activity well into Early Devonian. Perhaps the most important practical results of the Caledonian orogeny are massive

mature and multi-folded black alum shale deposits in Jämtland, Sweden and the possible allochton from the same or similar source at Sillamäe, Estonia. A preliminary comparison of these two argillites is already presented in Table 3. The rare metals patterns are very similar, and so are the surprisingly low oil yields achieved in Franz Fischer distillation. Impressive lithological and biostratigraphic differences between the West-facies and East-facies of a single Türisalu member argillite facies have been convincingly stressed by D. Kaljo [6]. The zero or strongly lowered oil yield has always been found to be directly correlated with thermal maturation of native black shale. There are many techniques for shale maturation measurement, but the simplest and easiest is certainly the popular Conodont Alteration Index (CAI) that can also be used with acritarch organic material. The apatite matrix is first removed with (acetic) acid and color measurement is carried out under a microscope. The characteristic CAI color ranges from 1 to 6 (or 8 for hydro-thermal maturation) are given in the following Table 4.

Table 4. **Thermal metamorphic grade ranges**

CAI	Approximate conodont color	Maturation temperature range, °C
1	Pale brown	50 to 80
2	Reddish brown	60 to 140
3	Dark gray-brown	110 to 200
4	Dark gray	190 to 300
5	Black	300 to 480
6	Pale gray	360 to 550

In Sweden the conodont samples from three near zero oil yield black shales had the following CAI values: 5 to 8 (300 to >550 °C) for Hunneberg alum shale, 3 to 4 (110 to 300 °C) for the Fläsjö area in Jämtland (Järvsand and Kalkberget) and 5 (300 to 480 °C) in the southernmost Skåne [17]. All these shales had undergone severe orogenic maturation and some were clearly allochtonous [18, 19]. The unaltered autochtonous black shales with normal oil yield of 2.7 to 5.5 % can be found in Närke, Dalarna and Öland with CAI values 1 to 1.5. However, on Bornholm at the borderline between Baltica and Avalonia, the orogenic heating of the local black Dictyonema shale reached CAI value of 3.5 or 190 to 200 °C [20].

The surprising abrupt fall in the oil yield in the middle of a contiguous Türisalu member is not the only problem with Sillamäe argillite. In the nearby Orasoja member of the same facies the wrong order of the first appearances of the conodont *C. Angulatus* and the graptolite *R.f.multithecata* is considered extraordinary [21].

Considering all these contradictions a simple solution, emplacement of orogenic allochtons presents itself. The mudstone organic matter is extremely fine and moves easily with water across the comparatively flat cratonic surface. Some orogenic material may easily travel further than to Jämtland.

In contrast to Norway, where Caledonian orogeny caused significant heating to 150–200 °C of the Lower Cambrian, the Lontova formation clay and silt temperature has never exceeded 35 °C in Estonia [4]. In these measurements acritarch CAI values were used. The conodont CAI values for the Orasoja member just below the Türisalu member the CAI values, are 1 to 1.5 which means no thermal maturation, but the part of the Cambrian Rannu member has CAI = 2 [21] that suggests thermal maturation, hydrothermal metamorphic changes, or influx of sand and clay with fossils included from orogenic areas.

Toward the end of the last century, the recognition of lithological folding and faulting, both synchronous with and subsequent to thrusting, has provided further insight into the mechanisms of emplacement of vast allochtons [22] which need not be just clay and sand, but can as well be valuable ores for the production of such strategic materials like uranium, molybdenum and rhenium.

The metalliferous organic component of the anoxic black mud can actually be much older than the newly inhabiting fossils and it has to be thermally mature because of the orogenic origin. There has been much discussion about the Late Cambrian – Early Ordovician Orogeny (520 to 480 Ma) that introduced the Scandinavian Caledonides and supplied both Scandinavia and the Baltica with gigantic amounts of metalliferous anoxic black mud from Iapetus that was squeezed to death between Baltica and Laurentia. Two samples from the Kalak Nappe Complex (KNC) have been recorded. The timing of this metamorphic event with Ar-Ar inverse isochrone age as 498±13 Ma and 506±17 Ma just during the Türisalu/Varangu formation [15, 16].

Nuclear magnetic resonance (NMR) study of shale oil

In order to solve the contradictory problem of the thermal history of not the facies and not the fossils, but of the shale organic matter itself, the shale oils had to be studied for their thermal history.

In thermal decomposition of solid fossil fuels (coal) the main single product is toluene. The first to go are long-chain alkyls. Therefore a good quantitative measure for fossil fuel thermal maturation is change in the methylene/methyl CH_2/CH_3 ratio. For a mixture of thousands of compounds, usual analytical procedures like optical spectroscopy, mass-spectrometry or chromatography cannot be used, but the functional group ratios can be quantitatively precisely measured by modern very high field nuclear magnetic resonance (NMR) [23] in combination with various forms of heteronuclear single- and multiquantum correlation spectrometry through the $^1H - ^{13}C$ spin-spin couplings, collected into single Attached Proton Test (APT) suite in the Bruker TopSpin 1,3 software package [24]. A very high field 18.8 Tesla superconducting very low temperature (2 K with pumped

helium) high resolution magnet was used with total, multichannel digital frequency synthesis and measurement with a AVANCE III 800 MHz spectrometer. A total separation between the CH_2 and CH_3 groups was achieved with a clean cutoff between them at 21.8 ppm from TMS. A very significant difference was found between the native black shale oil samples. In the Maardu sample one methyl (CH_3) group was connected on average to 1.595 methylenes (CH_2), but in the Sillamäe sample only to 0.625 methylenes. The 2.5-fold difference shows that the Sillamäe argillite has survived orogeny and is thermally mature. Such maturation can not have happened at Sillamäe. The organic material appears to be endogenic with an orogenic source.

Considering the very impressive similarity between the chemical composition which involves not just Mo, U, V, Ni and Zn, but also Sb, As of different origin, it is very likely that we have at Sillamäe and Jämtland samples of the same allochtonic material in very different lithological settings and containing some more recent fossils.

It is also obvious from Table 2 that Estonian argillites are not really fossil fuels (carbon enrichment is only 600 or 700 Earth crust clarkes) but rather at Sillamäe at least, a valuable metalliferous ore with molybdenum enrichment equal to 800 clarkes. Future technologies might be wise to consider these circumstances. It must also be stressed that the idea about selective influx of new endogenic material to some severely denuded locations in the Estonian argillite formations has already been proposed by Valter Petersell [14].

Technological choices

It is obvious that Estonian argillites are very different from the kukersite. Argillites are not uniform even in a single formation and very significant chemical diversity is hiding in seemingly similar formations. Thus the technologies for future use of such non-uniform ore must also be diverse and flexible.

Most technologies for the production of rare metals from various ores or fuels involve extraction at some stage of the process. Extraction must always be optimised for a compromise between product yield and the least possible pollution caused by waste dumps and the cost of closing the factory installations. Therefore metals extraction from the pretreated argillite material merits serious attention.

Our experiments with the Maardu black argillite without a metamorphic thermal history which is typical for the alum shales from the Scandinavian Caledonides, provided encouraging first results with mildly preroasted samples. Room temperature leaching with pure water provided a 45% soluble uranium yield after roasting at 500 °C, a 33% molybdenum yield after preroasting at 700 °C and a 13% vanadium yield after sample burning at 800 °C, all without any chemical additives [25]. This unusual solubility is

caused by the presence of unusual U(IV) in a sample of anoxic origin in a hydrated complex with phosphate as $UAl_8 (HPO_4)_8^{+12}$. This process was invented by Kurt Lupander, but described only in Ranstad company reports [26]. Still, it merits further attention. The only metals that are valuable enough to separate from shale are Mo, U, (V) and perhaps also the very difficult but very valuable Re. The results of Lupander show that with 1 h boiling water leaching a 79% yield of U is possible if roasting takes place at around 550 °C with sharp cutoff at 600 °C due to metal silicates formation. Unfortunately, this temperature is too low for organic matter gasification for further Fischer Tropsch synthesis, but low-temperature burning in a circulating bed is possible for fine (< 1 mm) material [10]. Conversely, some sort of thermal solution/hydrogenation Bergius or related process is possible, but losses would be large and yields low in comparison with coal liquefaction [27]. The metals extraction and oil production from the same shale appears to be incompatible.

Conclusion

In Estonia, allochtonous mature black argillites, actually mudstones, in the Eastern facies of the Türisalu formation from Toolse to Orasoja with the center at Sillamäe form the best source for a Mo, U, V, Re production. The preroasting can provide environmentally clean process heat.

Acknowledgment

REFERENCES

1. *Raukas, A.*, *Teedumäe, A*. (eds.). Geology and Mineral Recources of Estonia. – Tallinn: Estonian Academy Publishers, 1997. 436 P.
2. *Gee, D. G.*, *Sturt, B. A.* (eds.). The Caledonide Orogen: Scandinavia and Related Areas. – Chichester, UK: John Wiley&Sons, 1985. 1266 P.
3. *Voipio, A*. (ed.). The Baltic Sea // Elsevier Oceanography Series. Vol. 30. – Amsterdam: Elsevier, 1981. 405 P.
4. *Kirsimäe, K., Jørgensen, P., Kalm, V*. Low-temperature diagenetic illite–smectite in Lower Cambrian clays in North Estonia // Clay Minerals. 1999. Vol. 34, No. 1. P. 151–163.
5. *McKerrow, W. S.*, *Mac Niocaill, C., Dewey*, *J. F*. The Caledonian Orogeny redefined // J. Geol. Soc. London. 2000. Vol. 157, No. 6. P. 1149–1154.

6. *Kaljo, D., Kivimägi, E.* Zonal stratigraphy of the Estonian Tremadocian // Graptolites and Stratigraphy / D. L. Kaljo, T. N. Koren (eds.). Tallinn: Estonian Acad Sci., Inst. Geology, 1976. P. 56–63.

7. *Kivimägi, E.* Hitherto unused recources of Estonia // Estonian Nature. 1974. Vol. 17, No. 4. P. 199–202 [in Estonian].

8. *Kallaste, T.* Inst. Geology of Tallinn University of Technology, Tallinn, 2009, personal communication.

9. *Lippmaa, E., Maremäe, E.* Uranium production from the local Dictyonema shale in North-East Estonia // Oil Shale. 2000. Vol. 17, No. 4. P. 387–394.

10. *Puura, V.* (ed.). Geology and Mineral Resources of the Rakvere Phosphorite-bearing Area. Inst. of Geology of Acad. Sci. of the Estonian SSR. Geological Survey of the Estonian SSR. – Tallinn: Valgus Publishers, 1987. 211 P. [in Russian]

11. *Lide, D. R.* CRC Handbook of Chemistry and Physics. – New York: CRC Press, 2001. P. 14–17.

12. *Strandell, E. A.* (ed.). Uranium production from ore at Ranstad, 40 years of developing uranium extraction from Swedish alum shale. 1998, Ranstad TPM 1534. 536 P. [in Swedish].

13. *Andersson, A., Dahlman, B., Gee, D. G., Snäll*, S. The Scandinavian Alum Shales. – SGU Ser. No. 56. 1985. 50 P. (CERI-mines, Continental Precious Metals Inc. 2009).

14. *Petersell, V.* Dictyonema shale // Estonian Combustible Natural Resources and Wastes. 2006. No. 1. P. 8–9 [in Estonian].

15. *Kirkland, C. L., Daly, J. S., Chew, D. M., Page, L. M.* The Finnmarkian Orogeny Revisited: An isotopic investigation in Eastern Finnmark, Arctic Norway // Tectonophysics. 2008. Vol. 460, No. 1–4. P. 158–177.

16. *Roberts, D.* The Scandinavian Caledonides: Event chronology, palaeographic settings and likely modern analogues // Tectonophysics. 2003. Vol. 365, No. 1–4. P. 283–299.

17. *Bergström, S. M., Löfgren, A., Maletz, J.* The GSSP of the second (upper) stage of the Lower Ordovician series: Diabasbrottet at Hunneberg, Province of Västergötland, Southwestern Sweden // Episodes. 2004. Vol. 27, No. 4. P. 265–272.

18. *Löfgren, A. M.* Reinterpretation of the Lower Ordovician conodont apparatus *Paroistodus* // Palaeontology. 1997. Vol. 40, Part 4. P. 913–929.

19. *Löfgren, A.* Conodont faunas with *Lenodus variabilis* in the Upper Arenigian to Lower Llanvirnian of Sweden // Acta Palaeontol. Pol. 2003. Vol. 48, No. 3. P. 417–436.

20. *Stouge, S., Rasmussen, J. A.* Upper Ordovician conodonts from Bornholm and possible migration routes in the Palaeotethys Ocean // Bull. Geol. Soc. Denmark. 1996. Vol. 43. P. 54–67.

21. *Heinsalu, H., Kaljo, D., Kurvits, T., Viira, V.* The stratotype of the Orasoja member (Tremadocian, Northeast of Estonia): lithology, mineralogy and biostratigraphy // Proc. Estonian Acad. Sci. 2003. Vol. 52, No. 3. P. 135–154.

22. *Gee, D. B., Juhlin, Ch., Pascal, Ch., Robinson, P.* Collisional Orogeny in the Scandinavian Caledonides (COSC): Proposal for an International Continental Scientific Drilling Program, 07. April 2009.

23. *Grant, M., Harris, R. K.* (eds.). Encyclopedia of Nuclear Magnetic Resonance. Vol. 1–9. – Chichester UK: Wiley, 2002. P. 6184.

24. Bruker Corporation, Almanac 2009, AVANCE III TopSpin.

25. *Althausen, M., Maremäe, E., Johannes, E., Lippmaa, E.* Weathering of metalli-ferous alum shales // Proc. Estonian Acad. Sci. Chemistry. 1980. Vol. 29, No. 3. P. 165–169.
26. *Lupander, K.* Preliminary studies on alternative processes for uranium extraction from ore using roasting as a pretreatment method I, II // TPM KFF-4, TPM KFF-5. Ranstad, 1961 [in Swedish].
27. *Krenkel. H., Bromley-Challenor, M., Snäll, S.* Evaluation of liquid hydrocarbon recovery potential from Swedish alum shale // International Oil Shale Symposium 8–11 June 2009, Tallinn, Estonia.