

## RESOURCES, PRODUCTION AND PROCESSING OF BALTO-SCANDIAN MULTIMETAL BLACK SHALES

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*It has been generally accepted that black shales are oil shales and have to be handled as sources of fuel oil. This attitude has been so prevalent that it is applied even to those thermally mature black shales in Jämtland (Sweden) and Sillamäe (Estonia) that supply practically no oil on thermal treatments even in the presence of hydrogen. It may well be that these shales are a very significant source not for oil and not only for uranium, but for valuable metals in general, including molybdenum, rhenium and many others. A new, hydrogenation-based technology may be necessary in this case.*

### Introduction

The multimetal sediments around the Baltic Sea are black shales (argillites) which were formed in Upper Cambrian and Early Ordovician time. These sediments are of diverse origin and thermal history. The Scandinavian highland region experienced major tectonic disruptions that spread allochthonous material long distances and intermingled with autochthonous sediments. The total amount of available black shales is truly immense, and the list of accumulated valuable minerals therein is long. The accumulation of these metals has been very selective and some Clarke values concerning Earth crust are impressive. The values at Sillamäe are 95 for U, 191 for Re and 817 for Mo.

At the recent June 2009 International Oil Shale Symposium in Tallinn, M. Bromley-Challenor from Continental Precious Metals stressed the potential availability in Sweden of 4.5 billion barrels oil from rock with a 10% organic matter cut off [1]. In a more detailed poster the same company [2] presented the HYTORT hydrogenation/thermal solution technology for oil production from the Viken deposit shales, and also stressed the multimetal potential of the spent shale that remains after generating about 5.5% of oil. The 163 km<sup>2</sup> Viken deposit NI-43101 is supposed to hold millions of tons of

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uranium in these thermally mature black shales that yield no oil by retorting or Fischer assay. The Aura Energy Ltd. 64 km<sup>2</sup> holdings in the same Viken area are just alongside with NI-43101. All this, together with Estonian black shales makes these rocks the largest known uranium resource in the European Union with a significant potential for other important industrial metals.

The Viken (and Sillamäe) black shales are tight structureless silty mudstones wherein the metals are tightly bound into metalloporphyrins and other stable organic structures. Unfortunately these organic structures are low in hydrogen, and thus retorting oil yield is very low or nil even in many cases where the organic carbon content is >10%. Typical examples are not only from Jämtland and Sillamäe, but also from Scåne and Hunneberg. The other extremes are the Närke, Ranstad and Maardu black shales that have reasonable Fisher assay oil yields (>5%), but are low in U, Mo, Re, Ni, V and Zn.

### Shale pretreatment options

The low oil yield from the Upper Cambrian/ Lower Ordovician black shales is caused not only by hydrogen deficiency in black shales, but also by competition between oil and coke formation on retorting. The oil yield is higher for the Närke and US Green River shale (2.1% H) followed by the Eastern Devonian US shale (1.6% H), the Ranstad and Maardu argillites (1.46% H) while falling close to zero for Jämtland and Sillamäe black shales (0.8% H). The missing hydrogen can be added at high temperature and pressure as gas or some cheap organic solvent, such as methanol. The Bergius process for direct conversion of coal to liquids was patented in 1913/1919 [3]. In this process, dry coal is hydrogenated, mixed with heavy oil recycled from the same process, and a cheap catalyst. Estonian shale oil turned out to be a welcome additive to the recycled reactive fluid [4], which is required to dissolve even the heaviest fragments being formed from the coal or oil shale organic matter (kerogen). The thermal solution process described by Krenkel *et al.* [2] for the Jämtland shales is actually the old Bergius-Pier process applied to black shales. It is now known as the HYTORT process [5] that can increase the shale retorting oil yield by hydrocracking/hydrogenation. The increase is 360% for Billingen (Sweden) shale, and 200% for Närke and 110% for Eastern US Devonian shales. There is an interesting contradiction between the new and older data. While Krenkel and Bromley-Challenor found a 6% oil yield in the thermal solution process for the Viken shale in Central North Sweden (14.5% org. C, 0.7% H), the Institute of Gas Technology in attachments to [5] about HYTORT-treatment of the very representative for the region drill hole Myrviken 78009 found zero oil yield both in conventional and the hydrogen-pressurized (1001.8 psig, 1014.6 F) retorting. In this connection a recent update of Economic Scoping Study [6] is highly relevant. The April 08, 2010 text

reads: “The (Viken, Sweden) shales contain a significant quantity of organic carbon which we considered extracting for its potential oil production. While these may still have potential, we have determined that the best way to add shareholder value and advance Multi Metal Sediment deposit Viken to production is by focusing on mining three key metals (U, V, Mo). This will also serve our goal of partnering with a major mining company on the property”.

The plans for Jämtland shale oil are thus abandoned for the time being. We can now turn our full attention to Caledonian precious minerals.

### **Caledonian precious minerals**

In the update to Economic Scoping Study [6] it is mentioned that alum shale metallurgy is very complex and does not respond well to preconcentration processes such as flotation. Recovering the targeted metals will require the application of hydrometallurgical techniques. Or to put it simply – in order to extract the insoluble precious metals, must we oxidize or reduce the ore? In any case we must break the porphyrin-related tetrapyrrole ring systems that chelate and capture the industrially important metals. Porphyrins are ubiquitous, have perhaps been found even in Orgueil and other meteorites and cosmic dust. Porphyrins have been located in an alpine oil shale long ago [7] and a comprehensive list of elements, including all the precious metals and materials participating in life process has been published by the Australian Government Analytical Laboratories AGAL [8]. This list includes Ag, Au, Cd, Ce, Co, Cu, Hg, Mn, Mo, Ni, Re, Zn, Zr, Th, U, V and Y as possible target metals for production from shales. All these AGAL metals are absolutely necessary for the life of some species. Tungsten W is rarely found in enzymes, but it is present in the active center of the tungsten-iron-sulfur enzyme acetylene hydratase of *Pelobacter acetylenicus*, a strictly anaerobic organism. All these metals form very stable chelates including all the isotopes of U and Th, and even the actinides such as Np and Pu. Generally, the heavier the central chelated atom, the stronger the complex as long as the ion remains small enough to fit the chelate cage. Many heavy metals (Re, U, Mo) only accumulate in shales because of a high affinity to the porphyrin ring. All black shales are surprisingly similar in their basic structure and the list of included precious metals. Just two groups dominate – Mo, Ni, Re, U, V and Ag, Bi, Cd, Cu, Se. The first group is porphyrin-bound at a molecular level, but the other group mostly forms distinct minerals. Obviously, the basic chemistry of life has not changed for eons.

On August 6 and 9, 1945 atomic bombs exploded over Japan. The nuclear era opened with an arms race and immediately involved Estonia. The United States produced carnotite, a mixed uranium/vanadium ore from 1873 which was also used by the Manhattan project together with later imports from Katanga. The Soviet Union began immediately in August 1945 with

preparations for uranium production in the occupied countries, Germany (Erzgebirge) and Estonia (Narva). SAG Wismut founded in June 1946 [9] was soon developed into the largest uranium-production facility in the world, producing altogether 230 000 tons of uranium of varied concentrations that were immediately transported into Soviet Union and 40% of it to Sillamäe, where mining of local uranium ore (black shale) and processing of various imported concentrates began in June 1948 at the factory No 7 [10]. The ore imported from Wismut originated about equally from black shales in Eastern Thuringia and the hydrothermal pechblende vein ore in Western Erzgebirge.

Shales and sedimentary ores were mined in different regions, including Sweden [11], Estonia [10], Canada and Central Asia. In Germany, there are still worth mentioning the Ronneburg/Gera mines, about which there are available extensive data [12] from deep drillings.

In Estonia even though the uranium-producing facility at Sillamäe was officially founded in June 1948, the preparatory experiments for using the uranium-rich Sillamäe-Narva region shales actually began during the 1944/45 winter in Narva at the former textiles-dyeing factory (Krasilnaya Fabrika). Building of the large production facility (Complex 4) began in 1947, and at first, up to November 1949 simple alkaline leaching of the carefully preroasted at 550 to 580 °C (<6 mm) crushed shale was used. This temperature optimizes uranium solubility up to 80% in plain water because it is sufficient for complete destruction of the porphyrine rings that chelate the heavy metals, but is still too low for the formation of insoluble uranium silicates [11, Figure 390 on p. 528; 13, 14]. From Nov. 1949 to July 1950 additional oxidation with  $\text{KClO}_3$  was used and a short experiment with soda alone failed. From Nov. 1950 a combined technique was introduced that began with alkaline chlorate treatment of the preroasted shale that was then leached at 60 to 75 °C with dilute (3–5 g/L) sulfuric acid, thereafter at a higher temperature (60 to 86 °C) with 2% soda and finally precipitated with sulfuric acid at pH 5 to 5.5. For the treatment of 1 ton of dry ore 96 kg soda, 56 kg of sulfuric acid, 4.6 kg of  $\text{KClO}_3$  and 2 kg of sodium hydroxide were used in 1950. The ore was of mixed origin. In the beginning, most of it was locally mined at Sillamäe (0.0274% uranium), but some came later from Thuringia and Erzgebirge (Object Maltsev) [10]. Only there is a combination of shale, pitchblende and pech possible.

Such a milling technique was also used at SAG Wismut in Eastern Thuringia and Western Erzgebirge area, where more than 90% of the uranium was produced by underground mining, although *in situ* leaching was also used. Milling was carried out hydrometallurgically by the same soda alkaline/acidic processes, mostly in Seelingstadt-Truenzig, but some ore was sent to Soviet Union with no treatment [15]. The uranium production by ore roasting with the following acid, alkaline or mixed extraction or *in situ* leaching (ISL) treated all other components of the ore as useless waste that was discarded in heaps or into the rivers and sea. This was wasteful and very polluting, although under the proper geological conditions

it is widely used. The long list of the components of Ronneburg ore is similar to the Sillamäe list with the exception of the missing molybdenum. The active strongly acid or alkaline lixiviant that is expected to dissolve and leach out uranium dissolves many other, often environmentally hazardous elements as well. Keeping the lixiviant underground for decades while keeping it from infiltrating into underground aquifers is not an easy task. To illustrate the matter, Table 1 provides fairly full borehole data for a typical Ronneburg, Thuringian graptolitic shale [12] and for the Sillamäe [16] and Toolse [17] uraniferous argillite. The more poisonous elements, such as antimony, arsenic, chromium, copper, lead, nickel, uranium and vanadium are all represented in these ores. Only radium is missing, because it is precipitated as insoluble sulfate. It is obvious that uranium production in the Soviet sphere was much more polluting and expensive than in the NATO domain. This political divide, together with the starkly disparate and conflicting end uses – military and peaceful clean energy, created a situation

Table 1. Borehole Samples

Component	Ronneburg 6175_89_375 [12]	Sillamäe [16]	Toolse [17]	Component	Ronneburg 6175_89_375 [12]	Sillamäe [16]	Toolse [17]
	<b>%</b>	<b>%</b>	<b>%</b>		<b>ppm</b>	<b>ppm</b>	<b>ppm</b>
SiO <sub>2</sub>	65.14	38.18	51.15	Gd	11.32		
TiO <sub>2</sub>	0.34	0.528	0.73	Ho	2.56		
Al <sub>2</sub> O <sub>3</sub>	6.98	9.11	9.76	La	45	43	
Fe <sub>2</sub> O <sub>3</sub>	4.50	6.95	8.03	Li	23		
MgO	0.96	1.32	1.08	Lu	1.05		
CaO	2.23	10.99	2.82	Mo	90.0	978	406
Na <sub>2</sub> O	0.13	0.06	0.09	Nd	44.7		
K <sub>2</sub> O	1.97	5.73	5.73	Ni	272	152	140
P <sub>2</sub> O <sub>5</sub>	1.616	0.566	0.39	Pb	56.8	178	120
MnO	0.021	0.138		Pr	10.5		
C <sub>org</sub>	9.40			Rb	72	88	
S	3.50	3.188	5.07	Re	0.203		0.18
				Sb	56.84		
	<b>ppm</b>	<b>ppm</b>	<b>ppm</b>	Se			4.3
Au			0.004	Sm	9.9		
Ag	6.84			Sr	87	60	
As	89.0	118	38	Te			0.1
Ba	949	360		Tb	1.78		
Bi	0.20			Th	5.6	2	14.5
Cd	1.37			Tl	2.54		
Ce	46	54		Tm	1.08		
Co	8.8	6		U	41.5	255	162
Cr	205			V	3414	892	1040
Cs	4.70			Y	92	45	
Cu	285	202	75	Yb	7.05		
Dy	11.8			Zn	47		170
Er	7.76			Zr	121		
Eu	2.40						

where the price of uranium could not be analyzed and predicted through the usual projective scenarios. The International Atomic Energy Agency analysis of uranium supply to 2050 [18] proved to be totally wrong and was of no use in planning and building production sites. The usual predictive demand-limited mechanism does not work with uranium. A more stable approach might be provided by the use of some other precious metals in the shales, too.

### Breaking the porphyrin ring by hydrogenation

As mentioned before, the metals, both valuable and those in the waste, are not easily leachable because they are immobilized in porphyrin rings. These rings can be destroyed by oxydation, through roasting and burning, but what is less known is that hydrogenation can accomplish the same thing. Multiple hydrogenation destroys the aromaticity and thus the stability of the ring and makes the metals easily leachable.

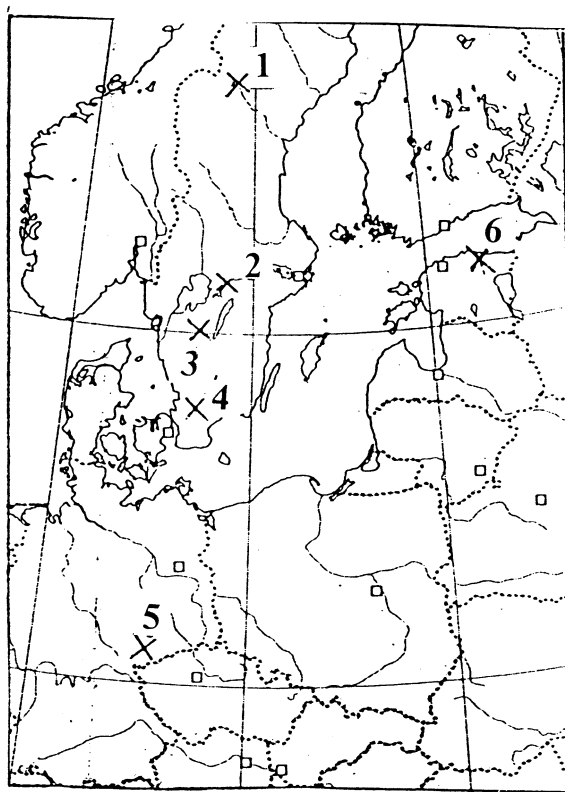
Using the Eastern US Devonian oil shales with only 13.7% organic carbon and 1.6% hydrogen, oil yield can be doubled by HYTORT process [5]. And not only that, the solubility of useful minerals is also increased very significantly (see Table 2), based on Oak Ridge National Laboratory data.

*Table 2. Sulfuric acid leaching tests on Eastern US Devonian oil shale*

Element	Element recovery from raw shale, %	Element recovery from HYTORT hydrogenated spent shale, %
Aluminum	39	77
Iron	21	99
Cobalt	35	100
Chromium	55	84
Copper	28	88
Manganese	59	92
Molybdenum	30	98
Nickel	35	97
Uranium	78	82
Vanadium	32	96
Zinc	76	94
Rare Earths	44	75

In the case of the Myrviken shale (Jämtland, Borehole 78004 and 78009, 70 to 80 meters) the oil yield is zero, even with HYTORT hydrogenation, but metals leachability is high. Minerals leachability depends upon other factors, namely the porphyrin chemistry. Metals solubility should parallel that for the Devonian shales. After all, the porphyrins are very stable compounds that have been found in “much older Esthonian fire shales” [7, 19]. It

is well known that metal-chelated porphyrin rings can be electrolytically hydrogenated first to chlorins and thereafter desintegrated, freeing the chelated metals, such as uranium, vanadium and nickel [20, 21]. The method worked well with Venezuelan crude bitumen suspension and could presumably be combined with electrically heated hydrofragmentation technology, much used in shale gas technology. It might also work with black shales, enhancing their leachability. Of course, Sillamäe and Jämtland ores are similar, but not identical. Obviously, a detailed study of the Sillamäe ore must be carried out as in the paper [22]. This study must cover all the significant elements and although it is too early for large-scale use of the abundant black shales, the gigantic size of this world resource should not be ignored for long.



*Fig. 1.* Locations of the shale deposits in Europe. Sweden 1. Jämtland (Viken, Myrviken deposits), 2. Närke (Närke), 3. Västergötland (Hunneberg, Ranstad), 4. Scane (Scane). Germany 5. Thuringia (Ronneburg, Erzgebirge deposits). Estonia 6. (Maardu, Toolse, Sillamäe deposits).

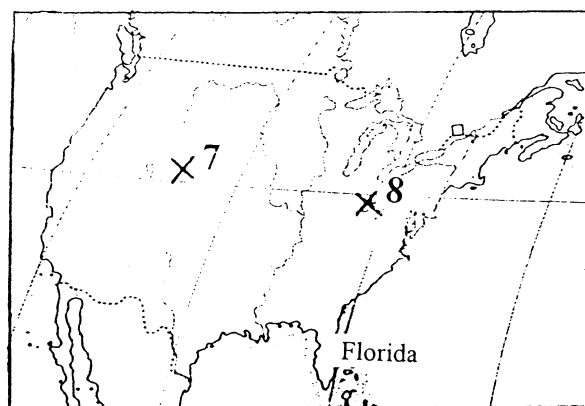


Fig. 2. Locations of the shale deposits in the United States. 7. Wyoming, Utah, Colorado (Green River deposit), 8. Ohio, Kentucky, Indiana, Tennessee (Eastern U.S. Devonian).

## Conclusions

It has been established that in black shales metals are tightly bound into very stable organic structures like metalloporphyrins. Aromatic porphyrin rings can be destroyed not only by oxidation but also by hydrogenation. Multiple hydrogenation destroys the stability of the ring and makes the metals easily leachable thereby increasing the yield of metals in hydrometallurgical processing.

Mentioned organic structures are often low in hydrogen and thus retorting oil yield is very low or even nil. It is now established that hydrocracking/hydrogenation process can considerably increase also the shale oil yield.

Black shales represent a significant source for future producing of oil and valuable metals (U, Mo, Re, V, and others).

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