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CHEMICAL WEATHERING OF LOWER PALEOZOIC BLACK SHALES OF SOUTH SWEDEN

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Lower Paleozoic black shales are widespread in Sweden and form part of the Baltic paleobasin, which deposits are also known in Estonia and the Leningrad Oblast of Russia. These rocks are enriched in a carbon substance and characterized by the significant content of uranium, vanadium, molybdenum, copper, nickel, cobalt, zinc, and lead.

Black shales contain high levels of Sr – 968; Ba – 337; U – 229; V – 509; Mo – 165; Zn – 411; Ni – 214; Cu – 112 (ppm) in secondary minerals composition formed on their surface.

Retrograde diagenetic conditions facilitate the black shales chemical weathering. Elements of the first (U), second (Mo, Sr, Zn), and third (V) hazard classes are washed out of black shales and secondary minerals and can further enter biological cycles.

Key words: black shale, geochemistry, chemical weathering, secondary minerals, mobility of chemical elements

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Introduction. Black shales (BSh) are widespread in the heterochronous paleobasins throughout the world. These rocks are enriched in a carbon substance and characterized by the significant content of uranium, vanadium, molybdenum, copper, nickel, cobalt, zinc, and lead [1, 2, 4-6, 14-16, 18, 20, 21, 24]. Lower Paleozoic black shales are widespread in Sweden and continue the dictyonema shale horizon of the Lower Ordovician Kopor suite, extending from the Leningrad Oblast through Estonia to Sweden.

For centuries, black shale has been one of the most important ores in Sweden. Since the XV century, alums have been actively extracted from black shales for paper and fabrics bleaching and leather processing. In the XX century, these rocks became a source of kerogen, radium, uranium, and rhenium [3, 17, 23]. The deposit exploitation led to the disturbance of rocks bedding and the occurrence of numerous quarries, which near-surface conditions promote active physical, chemical and biological weathering of black shales. The most active process is chemical weathering accompanied by the formation of crusts, cracks, and individual crystals of secondary minerals in water seepage areas.

Identification of geochemical features of BSh weathering and assessment of black shales composition inheritance by secondary minerals are crucial tasks.

Samples and analytical techniques. Samples were collected during the long-term fieldwork of the Department of Geochemistry of SPBU in South Sweden in cooperation with the staff of the Örebro University (Fig.1). Black shales were sampled layer by layer through the section. Secondary minerals (SM) were selected separately in colour to reveal their mineral and chemical composition with reference to BSh substrate.

A macroscopic description and petrographic studies of BSh and secondary minerals have been carried out. The mineral composition was analysed using the SPBU resource centres equipment: X-ray analysis (Rigaku MiniFlex II), Raman spectroscopy (Horiba LabRam HR800), quantitative analysis of organic carbon (Euro EA3028-HT), SEM and EMPA (TM 3000 Hitachi, Carl Zeiss Merlin). The composition of BSh and SM was studied using ISP-MS (ELAN-6100 DRC from PERKIN ELMER and Agilent 7700x) in VSEGEI.

The experiment on the pore solution extraction from BSh was also conducted in VSEGEI. The rock was crushed and abraded to a particle size of 74 μm (200 mesh) for sample averaging, pores and microcracks opening in order to ensure the access of extractant to free and mineral-based salts and colloidal particles. Extraction was carried out by dilution process with rock/water ratio of 1:10 by the procedure described in [8-10]. The weight content of the submicron fraction was determined

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by the gravimetric procedure from aliquot obtained after filtration of the colloidal salt solution [7, 11, 12]. The chemical composition of the solution was determined by the ICP-MS.

The experiment on the SM solubility dynamics estimation was carried out in the SPBU resource centre within 24 days with the subsequent ISP-MS analysis. The powdered sample was filled up with water, the flasks were placed in a thermostat on a vibrating table for constant mixing. Aliquots were taken at 1, 3, 6, and 10 hours and then after 2, 6, 9, 13, and 24 days. In solutions, pH and chemical composition were determined [22].

Geological and mineralogical characteristics. The largest number of BSh deposits is located in South Sweden, Närke (Kvantorp and Latorp), Billingen, Kinnekulle, Hållberg, Hanneberg, Skåne areas, and Åland Island (Fig.1).

Black shales occur on the Lower Cambrian sandstones being overlapped by Ordovician limestone. The layer thickness varies from a few meters to 20 meters. The shales are characterized by black colour and thin-layered texture. The rock consists of 50-85 % clay particles (hydromica, kaolinite, smectite, chlorite), 10-40 % allothigenic silt-sized minerals (quartz, K-feldspar with admixed biotite, muscovite, and amphibole), and 5-25 % organic carbon. There are also authigenic concretions of different composition given in descending abundance order: carbonate (anthraconite), sulphide (pyrite), silicite, and phosphate.

Carbonate concretions are of occurre frequently, lenticular-shaped and reach the size of 0.7×1.5 m. The carbonate fine-grained cores with rare sulphide inclusions are rimmed by mega grained calcite-anthraconite. Sulphide concretions are found in the microforms and even individual pyrite crystals with chalcopyrite and sphalerite impurities. Siliceous concretions up to 1 mm in size are composed of chalcedony and are clearly visible in petrographic sections. Phosphate oolites are rare, although high phosphorus concentration is commonly recorded in the rock composition.

Scanning electron microscopy and electron microprobe analysis confirmed the significant content of silty-psammitic admixture, as well as the presence of authigenic gypsum and other aqueous sulphates (Fig.2).

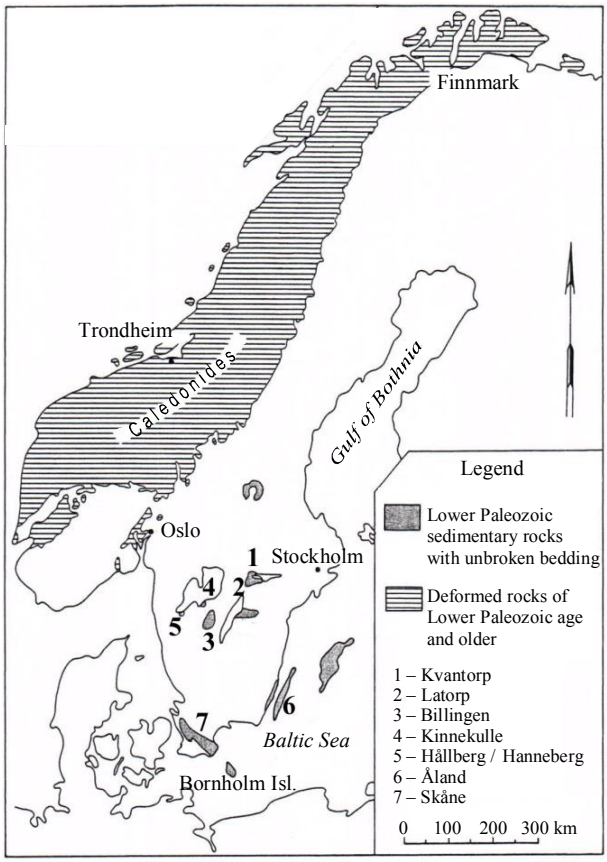


Fig.1. Distribution of Lower Paleozoic rocks in Scandinavia [13, 23]

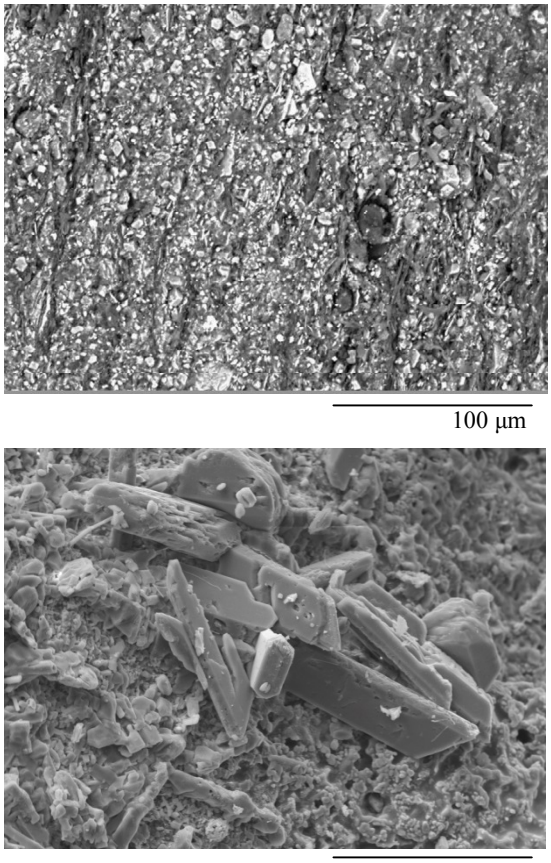


Fig.2. SEM image of gypsum crystals in black shale

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Geochemistry of black shales. A wide range of trace elements is presented in the Sweden black shales composition (Table 1).

Table 1

Trace elements composition in black shales of South Sweden, ppm

Element	Mean value (n = 53)	Standard deviation	Maximum value	Abundance [19]	Enrichment factor (mean / abundance)
U	82.6	47.9	216.0	9.9	8.35
Th	8.5	3.2	17.3	7.8	1.09
V	578.5	235.5	1410.0	180	3.21
Mo	175.2	71.4	411.0	14	12.52
Cu	61.2	44.0	181.0	140	0.44
Co	8.5	9.4	39.6	18	0.47
Ni	49.2	40.2	186.3	67	0.73
Pb	35.8	34.8	198.0	25	1.43
Bi	0.4	0.1	0.7	1.8	0.22
Zn	54.3	57.6	381.0	160	0.34
Sb	6.3	3.3	15.9	5.3	1.18
Cd	0.7	0.6	3.5	6.2	0.12
Tl	11.5	5.2	31.5	2.2	5.22
Ga	20.8	5.3	30.4	17	1.22
Ge	1.2	0.3	2.5	2.5	0.48
Sc	9.7	2.9	21.4	5.7	1.71
Cr	85.8	41.1	160.0	93	0.92
Rb	153.8	49.9	281.0	76	2.02
Cs	12.3	7.3	46.8	4.2	2.92
Sr	74.0	36.2	239.7	230	0.32
Ba	722.5	928.0	6720.1	630	1.15
Be	3.2	0.8	5.5	2.6	1.25
Ce	65.0	18.7	96.0	55	1.18
Y	15.9	8.1	43.2	23	0.69
Re	0.1	0.03	0.2	0.8	0.11

BSh are characterized by high contents of U – 82.6; V – 578.5, and Mo – 175.2 (ppm). The 12.5 enrichment factor for Mo, 8.3 for U, and 3.2 for V show that element contents are significantly higher than the abundances.

Mobile element forms in black shales were determined by chemical fractionation. The experiments have shown that the water-soluble fraction content in BSh varies from 0.2 to 3.6 wt%. After water extraction, the water-soluble form was analyzed by the ICP-MS (Table 2).

Table 2

Trace elements composition of an aqueous extract from black shales, ppm

Element	Mean value (n = 53)	Standard deviation	Maximum value	Enrichment factor (mean content in an aqueous extract / mean content in rocks)
U	346.2	641.4	2460	4.2
Th	2.2	5.0	27.3	0.3
V	125.5	216.6	1090	0.2
Mo	182.6	649.1	4020.2	1.0
Cu	228.2	381.9	1590	3.7
Co	136.5	183.9	922	16.0
Ni	779.8	1076.4	6040	15.9
Pb	2.3	5.4	29.7	0.1
Bi	0.1	0.2	0.8	0.1
Zn	258.9	210.3	1200	4.8
Sb	13.8	31.5	136.0	2.2
Cd	7.1	8.8	52.5	9.7
Tl	17.3	24.3	119.0	1.5
Ga	1.3	3.0	19.6	0.1
Ge	1.3	1.8	9.5	1.1
Sc	16.9	19.3	103.0	1.7

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Element	Mean value (n = 53)	Standard deviation	Maximum value	Enrichment factor
Cr	13.7	13.1	60.4	0.2
Rb	125.2	128.1	599.0	0.8
Cs	11.2	15.6	71.3	0.9
Sr	221.2	239.5	1290	3.0
Ba	137.3	209.3	1000	0.2
Be	6.4	5.8	37.5	2.0
Ce	60.8	78.5	393	0.9
Y	47.5	85.7	454	3.0
Re	0.5	1.1	5.7	5.5

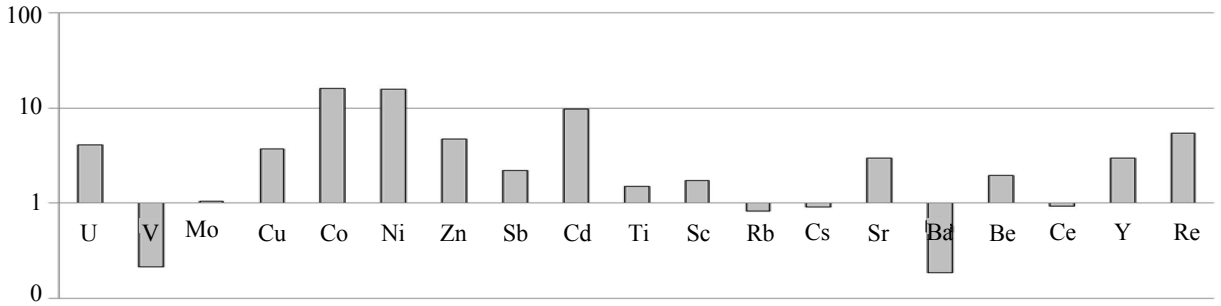


Fig.3. Enrichment factors of trace elements in aqueous extracts of BSh relevant to

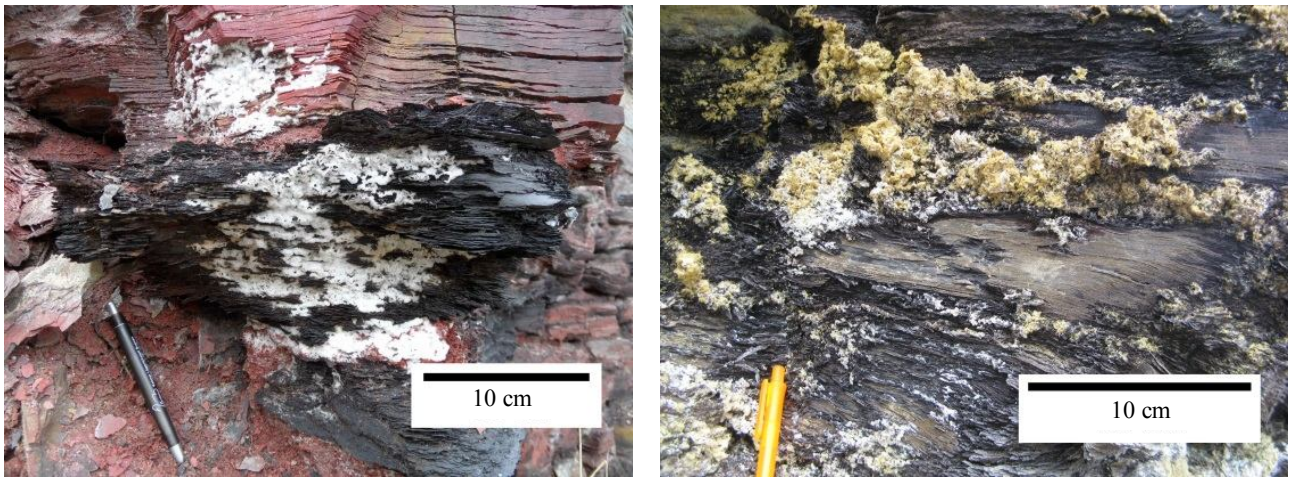


Fig.4. Secondary minerals as a product of black shales chemical weathering

The experimental results have shown significant contents of Ni, Mo, and U (up to 6040, 4020, and 2460 ppm, respectively) in mobile water-soluble form.

To illustrate the presence of the water-soluble phase in BSh, the enrichment factor was calculated as the ratio of the element content in the aqueous extract to the content in BSh. The calculations find that cobalt, nickel, cadmium, zinc, and uranium (enrichment factor varies between 4 and 16) predominate in water-soluble form. Whereas molybdenum and vanadium accumulate mainly in the bulk sample, being washed out of the rock to a lesser extent (Fig.3). However, high maximum values of the element concentration in aqueous extracts are ubiquitously detected. For example, in a number of samples, molybdenum and vanadium forms are predominantly water-soluble. The alkalinity/acidity index was calculated as the Ce/Y ratio and estimated as 4.1 for BSh, sharply decreasing in water extract (1.3).

Chemical composition of secondary minerals. Secondary minerals formed on BSh surface in the weathering zone have lamellar and acicular crystal form and predominantly white and yellow colour (Fig.4). They are actively formed on the shale surface in schistosity and fracturing zones (zones of mechanical weathering), easily accessible for water seepage. This explains why the Swed-

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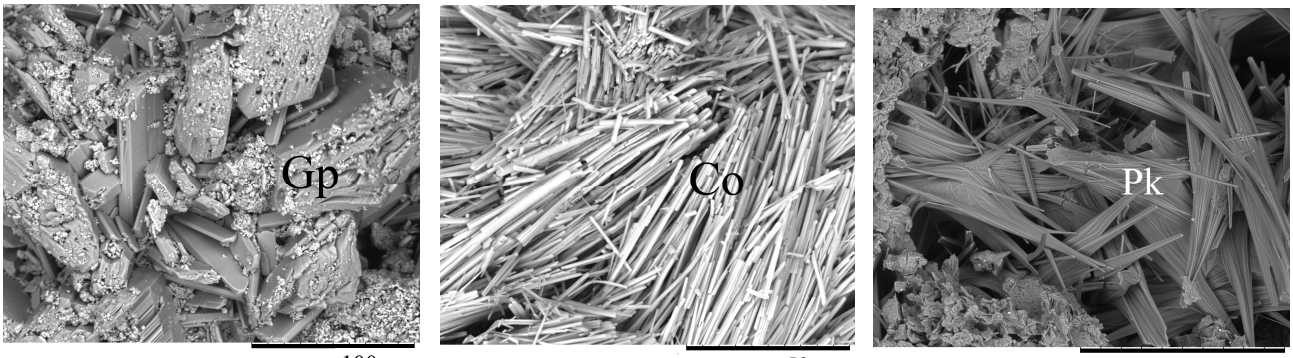


Fig.5. SEM images of secondary minerals

ish black shales were used for the extraction of alum and are also known as «alum shales». The alum extraction process included preliminary hot water roasting of BSh, followed by evaporation and crystallization.

Phase composition of secondary minerals was determined by XRD analysis and Raman spectroscopy. The following mineral phases were detected: gypsum ($CaSO_4 \cdot 2H_2O$), pickeringite ($MgAl_2(SO_4)_4 \cdot 22H_2O$), and small amounts of copiapite ($Fe^{+2}Fe_4^{+3}(SO_4)_6(OH)_2 \cdot 20H_2O$) and tamarugite ($NaAl(SO_4)_2 \times 6H_2O$) (Fig.5). At the same time, either gypsum with copiapite (in most samples) or pickeringite with tamarugite predominate in different samples. However, it is possible to distinguish between these two associations only in high magnification (Table 3).

Table 3

List of secondary minerals

Abbreviation	Mineral	Mineral Formulae
Gp	Gypsum	$CaSO_4 \times 2H_2O$
Pk	Pickeringite	$MgAl_2(SO_4)_4 \times 22H_2O$
Co	Copiapite	$Fe^{+2}Fe_4^{+3}(SO_4)_6(OH)_2 \cdot 20H_2O$
Ta	Tamarugite	$NaAl(SO_4)_2 \times 6H_2O$

Thus, the secondary minerals crystallized on the shale surface are products of the shale chemical weathering and are represented by alum group minerals.

Table 4

Chemical composition of secondary minerals. ppm

Element	Mean value (n = 15)	Standard deviation	Maximum value
U	49.4	67.2	229
Th	2.8	2.7	8.9
V	63	126.8	509
Mo	39.0	39.5	165
Cu	38.1	38.5	112
Co	9.0	11.7	39.6
Ni	50.6	63.8	214
Pb	2.7	2.7	9.9
Bi	0.1	0.01	0.1
Zn	66.7	121.3	411
Sb	0.6	0.6	2.5
Cd	1.1	1.3	4.4
Tl	3.5	2.4	9.7
Ga	4.0	4.5	15.6
Ge	0.2	0.1	0.4
Sc	1.6	2.1	7.6
Cr	10.9	14.5	44.4
Rb	15.8	26.2	109.0
Cs	1.2	2.6	10.5
Sr	280.7	275.1	968
Ba	46.6	82	337
Be	0.9	0.7	2.9
Ce	54.9	33	108
Y	20	15.2	67.9
Re	0.01	0.01	0.03

The content of the wide range of chemical elements was detected by ICP-MS analysis (Table 4).

The set of following elements have shown the highest concentration level (maximum values): Sr – 968; Ba – 337; U – 229; V – 509; Mo – 165; Zn – 411; Ni – 214; Cu – 112 ppm. The alkalinity/acidity index value is 2.7.

Secondary minerals undergo chemical weathering in retrograde digenetic conditions. To reveal the dynamics of SM dissolution, a model experiment on the solubility of samples of gypsum-pickeringite composition was carried out. The experimental conditions were close to the natural weathering. The experiment lasted 24 days, during which the trends of the solution pH (Fig.6) and element contents in gypsum (Fig.7) and pickeringite (Fig.8) samples were evaluated.

All the listed parameters changed under the experimental conditions.

Pickeringite solution showed significant changes in pH, becoming acidic, whereas gypsum solution pH varied from 5.2 to 6.9.

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The most elements showed increased concentrations in solutions in course of time. However, if for the gypsum solution the element concentration remained within the limits of thousandths milligrams per litre during the experiment, then in the pickeringite solution, it immediately increased to several milligrams per litre. The solubility curves of U, V, and Mo also differed from each other in diverse solutions.

This study showed sufficiently high dissolution rate of secondary minerals that could lead to the enhanced geochemical background in waters of the area.

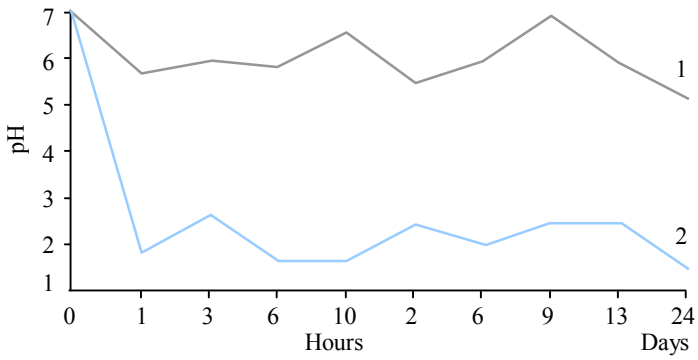


Fig.6. The change in the solutions pH of gypsum (1) and pickeringite (2)

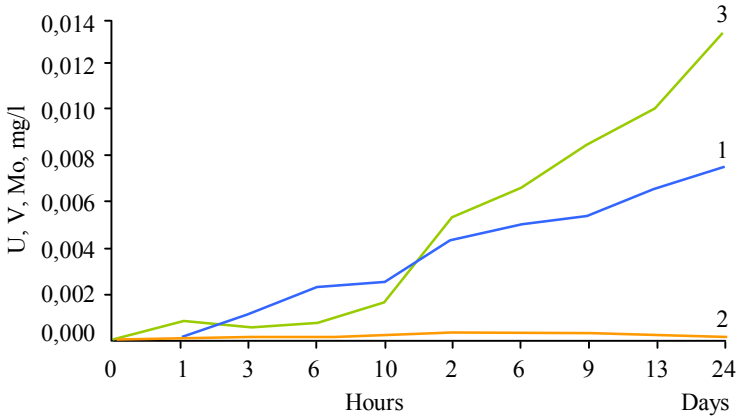


Fig.7. The change in U (1), V (2), Mo (3) content with gypsum dissolution

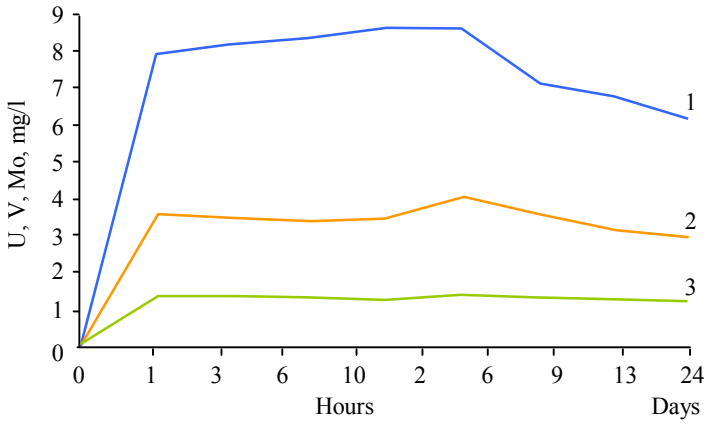


Fig.8. The change in U (1), V (2), Mo (3) content with pickeringite dissolution

Conclusions

1. A wide range of trace elements with a content level significantly exceeding the abundances was revealed in black shales composition. The highest enrichment factors are shown by Mo – 12.5, U – 8.3, and V – 3.2.

2. Some of the elements in BSh are in a water-soluble form, which content can reach 3 wt.%. The element enrichment coefficients in the aqueous extract relative to the bulk BSh are: Co – 16; Ni – 16; Cd = 9.7; Zn = 4.8; U = 4.2.

3. Black shales provide high contents of the Sr – 968, Ba – 337, U – 229, V – 509, Mo – 165, Zn – 411, Ni – 214, and Cu – 112 (ppm) in secondary mineral composition formed on their surface.

4. Retrograde diagenetic conditions facilitate the black shales chemical weathering. Elements of the first (U), second (Mo, Sr, Zn), and third (V) hazard classes are washed out of black shale and secondary minerals and can further be involved in biological cycles.

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