

## CHEMISM OF RADIOLARIAN LYDITES FROM THE BOHEMIAN MASSIF REGION

V. DUBANSKÁ<sup>a</sup>, A. DUBANSKÝ<sup>a</sup>, V. HEJL<sup>a</sup>, F. CHALUŠ<sup>a</sup>, J. KUBÁT<sup>b</sup>, M. MAŠTALKA<sup>c</sup>,  
P. PODRACKÝ<sup>a</sup> and P. POVONDRA<sup>a</sup>

<sup>a</sup> *Geological Institute,*

*Czechoslovak Academy of Sciences, 165 00 Prague 6*

<sup>b</sup> *Department of Coke and Gas Technology,*

*Prague Institute of Chemical Technology, 166 28 Prague 6 and*

<sup>c</sup> *Institute of Nuclear Physics,*

*Czechoslovak Academy of Sciences, 250 68 Řež*

Received May 13th, 1976

The composition of radiolarian lydites of proterozoic age from the Bohemian Massif was studied by means of classical methods of chemical analysis, X-ray diffractometry, and spectral, radiochemical, and electron microprobe analyses. The samples of the lydites were taken from the Barrandien region, the west part of moldanubicum, and the Železné Hory region. Silicites from the lydite-carbonate strata in Mořičov near Ostrov on the Ohře were studied as well. The lydites from the Bohemian Massif region are rocks composed predominantly of SiO<sub>2</sub> (α-quartz) — its content is higher than 96% (98% in average). As admixtures are present mainly clay minerals and relicts of the proterozoic biosphere. Attention was paid particularly to trace contents of organic substances (bitumens) and some metals of biogenic origin (vanadium, copper, and uranium). The spatial arrangement of some elements within the siliceous mass of the lydites was determined by means of electron microprobe. From the results of chemical analyses, interdependence between the vanadium, copper, and uranium contents were found, which allowed the lydites to be divided into two genetic groups. A method was worked out for the determination of very low contents of organic substances in the lydites (of the order of 10<sup>-4</sup> to 10<sup>-5</sup>%), based on pyrolysis gas chromatography.

Radiolarian lydites predominantly of upper proterozoic age are in the Bohemian Massif region (Czechoslovakia) abundantly developed, particularly in three geological regions: the Teplá-Barrandien region, the Železná Hora crystallinicum, and the contactly metamorphosed islands in the Middle-Bohemian pluton (so-called island zones). Their geological and geographical aspects have been described by several authors, particularly by Kettner<sup>1</sup>, Kodym<sup>2</sup>, Rodič<sup>3</sup>, Zoubek<sup>4</sup>, Petránek<sup>5</sup>, and Dubanská<sup>6</sup>. No geochemical study has been so far presented: some more detailed works are found in silica industry papers, dealing, however, only with the chemical composition and physical properties of lydites (Bárta and coworkers<sup>7,8</sup> and others).

As the terminology of silicitic rocks, including lydites, is not unique over the world, the term silicite is to be defined first. The authors denote by this term siliceous sedimentary rocks of chemo-

genic origin; it is used to distinguish these siliceous sediments from sedimentary rocks of clastic origin composed predominantly of quartz grains (the so-called "quartz sediments"). In silicites the admixture of the clastic or some other (*e.g.* silicate) cementation material must not exceed 10% (see<sup>9</sup>).

The term lydite usually designates a dark silicite containing organic residues. A more specific designation is sometimes used according to the nature of the organic residues — radiolarian lydites for instance. In this work we denote as lydites the organogenic silicites of marinogenic origin.

## EXPERIMENTAL

### Samples

The radiolarian lydites from the Bohemian Massif region were taken from 12 localities representing significant deposits of these rocks within the territory of Bohemia (from the Barrandien region, the west part of moldanubicum, and the Železné Hory crystallinicum). Studied were also silicitic rocks from the lydite-carbonate strata from Mořičov near Ostrov on the Ohře. The localities are henceforth referred to according to the names of the near-by settlements (Fig. 1). A list of the samples analyzed and of the pertinent localities is given in Table I.

### Analytical Methods

The contents of the various macro- and microelements was determined by the common methods of quantitative chemical analysis applied to chemical analyses of silicites<sup>10</sup>.

The contents of some trace elements (Cl, V, Cu, Ga, As, Sr, In, Sb, I, Ba, La, Sm, Eu, Dy, W, Au, U) were also determined by neutron activation analysis. The samples were irradiated by a neutron flow in a nuclear reactor  $10^{13} \text{ cm}^2 \text{ s}^{-1}$ , the duration of the sample activation was



FIG. 1  
Survey Map of the Localities

TABLE I  
List of the Localities and Samples

Sample No.	Locality (in brief)	Locality (in detail)	Sample description (in brief)	Remarks
1	Malá Doubrava S.E. of Chudenice	rocky wood at the S.E. hillside of Malá Doubrava	black-grey lydite with quartz veins	
2	Borovy S.W. of Přeštice	quarry on the right bank of the Úhlava river (outskirts of the settlement), at the road Borovy-Jino, near the elevation point 350-8	black-grey lydite closely interwoven with fine quartz veins	pyrite macroscopically apparent (rarely), enhanced content of carbonates
3	Zálesí S.S.E. of Přeštice	rocks about 600 m S.E. of the settlement at the road Zálesí-Vlčí	grey, strongly recrystallized lydite	
4	Vodokrtý N.E. of Přeštice	small rocks at the settlement outskirts, near the road Vodokrtý-Háje	black-grey lydite with fine quartz veining	
5	Starý Plzeňec S.E. of Plzeň	quarry (middle part) at the S. outskirts of Starý Plzeňec, in the N. side of the Radyně hill, about 1 km N.E. of the elevation point 565	light grey lydite with fine quartz veining	ample coatings of Fe (Mn) oxides
6	Starý Plzeňec S.E. of Plzeň	quarry (outer, west part) at the S. outskirts of Starý Plzeňec, in the N. side of the Radyně hill, about 1 km N.E. of the elevation point 565	light grey lydite closely interwoven with vein quartz	unlike Sample 5 only little coating of Fe and Mn oxides
7	Ostrá Hůrka W. of Starý Plzeňec	elevation point 411; rock near the N. side of the road Černice-St. Plzeňec, about 2-5 km W. of Starý Plzeňec	dark grey lydite with numerous, fine quartz veining	

8	Kyšice S. of Kladno	elevation "Za Doubkovou skalou", E. of the point 417.3; outcrops S. W. of the settlement	light, white-grey lydite	
9	Ládvi district of Prague 8	abandoned quarry at the N.W. hillside of the elevation Ládvi; point 355.0	dark grey lydite with fine quartz veins	
10	Šárka district of Prague 6	rocks on the right bank of the Šárka brook, opposite the hillside "Džbán"	pink — grey-pink lydite	
11	Šárka district of Prague 6	rocks on the right bank of the Šárka brook, 300 m N.W. of "Džbán"	black-grey — black lydite with ample graphite pigmentation	high content of bitumenous substances
12	Šárka district of Prague 6	rocks opposite the inn "Dívčí skok", on the right bank of the Šárka brook	black-grey — black lydite	
13	Mofičov E. of Ostrov on the Ohře	small rocks in the very settlement, about 600 m S.W. of the elevation point 434.6	black-grey lydite with both fine and pronounced quartz veins, appreciably stratified	
14	Sovolusky N.N.E. of Starkoč	small rocks near the S. boundary of the woods, at the right side of the road Sovolusky-Sovolusská Lhota; about 500 m S. of the outskirts of the settlement	dark grey lydite	
15	Zdechovice W.S.W. of Přelouč	boulders near the lane Zdechovice-Chvaletice, about 1.5 km of Zdechovice	light grey clay silicite with a brownish shade	the designation "clay silicite" follows from the results of this work, with regard to the high content of clay minerals
16	Zdechovice W.S.W. of Přelouč	boulders near the S. boundary of the woods, about 2 km from Zdechovice, at the lane Zdechovice-Chvaletice	light grey clay silicite with fine quartz veins	

3 minutes, the spectrum was measured by using a Ge/Li detector (error of determination was 5–10% rel.)<sup>11</sup>.

Uranium, thorium, and potassium were also determined employing gamma-spectrometry with a scintillation NaI(Tl) crystal (dimensions 45 × 50 mm, resolution for <sup>137</sup>Cs 8%). Approximately 200 g of the sample was used for an analysis. The spectra obtained were analyzed with a one-channel amplitude analyzer, set up of adapted functional units of Tesla. The characteristic photo-peaks of the isotopes followed were measured: 210–270 keV (ThB, RaB), 310–370 keV (RaB, MsTh2), and 1400–1520 keV (<sup>40</sup>K); this made it possible, under the common assumption of maintained radioactive equilibrium within the natural decay series, to calculate the concentrations of uranium, thorium, and potassium in the sample<sup>12</sup>.

The analytical data were processed on a computer by using the program GAMA<sup>13</sup>, which enables the obtaining of the concentration values for the elements followed along with the corresponding fundamental statistical parameters, the  $\chi^2$  values for the significance test for the differences of the individual measurements, and the measurement durations in the various spectral ranges necessary for a preselected accuracy of determination.

The semiquantitative spectrographic analyses were carried out on a quartz prism spectrograph Q-24 (Zeiss, Jena) with a graphite electrode; a.c. arc was applied using a generator ABR-3, current intensity for the recording of volatile elements 6A, for less volatile elements 10 A.

For the determination of trace amounts of organic substances, a method based on pyrolysis gas chromatography was worked out by Dubanská and Dubanský<sup>14,15</sup>. Gas chromatographs of Pye (Panchromatograph) and C. Erba (Fractovap 2400 V) with a flame-ionization detector were used. The chromatographic columns were packed with 10%wt. m-bis-(m-phenoxyphenoxy)-benzene on Chromosorb W (80/100 mesh) (Lachema, Brno). Argon served as the carrier gas (purity 99.95%), flow rate 35 ml/min, detector sensitivity  $3 \cdot 10^{-9}$  A, voltage at the detector 50 V.

Since very low contents of pyrolysis products of bitumens, present in the silicitic rock in trace amounts ( $\sim 10^{-4}$  to  $10^{-5}\%$ ), were to be determined, rather high portions of the samples had to be taken to analysis (5–10 g, grain size 0.2–0.6 mm). A specially modified pyrolyzer had to be developed for this task, too<sup>16,17</sup> (Fig. 2).

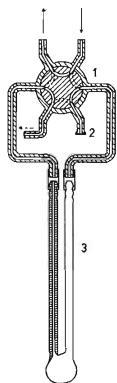


FIG. 2

Scheme of the Pyrolyzer Equipped with Six-Way Cock

1 Six-way cock, 2 closed outlet of the six-way cock, 3 pyrolysis vessel made of quartz glass; the solid arrow indicates the flow of the carrier gas, the dot-and-dash line shows the gas outlet during the evacuation.

The weighed amount was usually 5–10 g in the case of the silicites, batches as high as 50 g could be, however, pyrolyzed. For the analysis of the silicitic rocks, the (outer) diameter of the flask of the pyrolysis vessel should not exceed 16 mm (with the thickness of the quartz glass walls of 0.5–1 mm), for the heating to proceed in the optimum manner. The diameter of the tube providing the carrier gas inlet should not be greater than 4 mm; the tube served also for the filling of the sample. The pyrolysis products can be led to the chromatograph through the same tube or through a capillary. If a higher amount of water is released from the sample during the pyrolysis, it can be absorbed by magnesium perchlorate in a flask for hygroscopic substances.

In addition to pyrolysis, the bitumenous components were released from the rocks also by extraction with ethanol and benzene in a Soxhlet apparatus (volume 1 l) with a glass extraction insert equipped with a frit S1 (1100 g of analytically fine ground sample extracted for 1 h). The extracts were analyzed on a gas chromatograph attached to a mass spectrometer AEI-MS 902. Infrared spectra were scanned on a Beckman 4210 spectrophotometer. Packing columns were used for the chromatographic separation; silicon elastomer and Carbowax CX 20M (Gurr Ltd., London), 3% wt. on the carrier MV 2000, served as the stationary phases.

X-ray structural analyses applying the Guinier de Wolff method were performed by means of a microstructure apparatus RTG (Chirana, Prague) using  $\text{FeK}_\alpha$  radiation, and a diffractograph (Chirana) with the source Mikrometa 2 ( $\text{CuK}_\alpha$  radiation).

The distribution of chemical elements and the phase distribution (composition) at the polished sections of the samples studied were investigated by means of an electron microprobe JXA-50A (Jeol, Japan).

## RESULTS AND DISCUSSION

### *Chemical Composition of Radiolarian Lydites*

Results of chemical analyses, neutron activation analyses, and gamma spectrometry analyses of the samples are given in Tables II and III, those of the semiquantitative spectral analyses are given in Table IV.

The radiolarian lydites from the Bohemian Massif region were compared with similar silicitic rocks from the point of view of their chemical composition. Table V shows the results of analyses as reported in the literature (ordered chronologically according to the date of publication). In comparison with other silicites, Bohemian lydites are found to be relatively highly pure quartz rocks. This was confirmed also by X-ray structural analysis; in the X-ray diffraction patterns of the rocks analyzed, almost all the lines belong to  $\alpha$ -quartz, except for several indistinct lines, which we were not able to attribute (similarly as Forestier<sup>18</sup>).

Only in the samples from Zdechovice, clay minerals were identified as admixture. From the three prominent lines, some mineral (or a mixture) from the caolinite group was inferred to be present ( $d$  7.17,  $d$  4.22,  $d$  3.59)<sup>19</sup>. Regarding the possibility of overlapping lines of the clay mineral and quartz, we cannot give a closer specification of this mineral.

In addition to clay minerals, other aluminosilicates are present in the lydite samples as well, as follows from the contents of aluminium, calcium, magnesium, and alkali

TABLE II  
Results of Chemical Analyses of the Lydites (Samples No. 1–16)

Sample No.	Locality	SiO <sub>2</sub> %	TiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	MnO %	MgO %	CaO %
1	Malá Doubrava	98.23	0.005	0.25	0.43	0.004	0.01	0.04
2	Borovy	96.11	0.04	0.50	0.83	0.05	0.1	0.62
3	Zálesí	98.40	0.002	0.30	0.91	0.0004	0.03	0.015
4	Vodokrty	98.54	0.01	0.20	0.43	0.0008	0.03	0.01
5	Starý Plzenec	97.52	0.02	0.40	1.40	0.002	0.03	0.01
6	Starý Plzenec	98.65	0.02	0.20	0.74	0.0002	0.03	0.01
7	Ostrá Hůrka	97.93	0.02	0.45	0.98	0.002	0.08	0.02
8	Kyšice	98.26	0.02	0.35	0.81	0.004	0.04	0.02
9	Ládví	98.45	0.01	0.40	0.40	0.0003	0.04	0.01
10	Šárka	98.41	0.03	0.60	0.47	0.0009	0.04	0.03
11	Šárka	97.83	0.02	0.35	0.41	0.0006	0.03	0.02
12	Šárka	97.99	0.02	0.45	0.45	0.0008	0.03	0.02
13	Mořičov	96.21	0.05	0.40	0.60	0.0007	0.03	0.01
14	Sovolusky	98.83	0.005	0.35	0.24	0.001	0.02	0.01
15	Zdechovice	84.07	0.32	9.20	0.33	0.004	1.7	0.14
16	Zdechovice	85.45	0.28	8.10	0.87	0.006	1.6	0.1

TABLE III  
Results of Chemical Analyses of the Lydites (Samples No. 1–16)

Sample No.	V ppm	Cu ppm	Ga ppm	In ppm	Sb ppm	As ppm	La ppm	Sm ppm	Eu ppm	Dy ppm
1	100	12	0.1	0.006	1.0	1.0	1.0	0.1	0.02	0.2
2	300	37	1.0	0.001	1.5	1.3	4.0	3.0	0.7	4.0
3	300	35	0.5	0.004	3.5	3.0	2.5	1.0	0.2	1.5
4	180	24	0.3	0.004	5.0	6.0	8.0	1.0	0.2	1.5
5	260	63	4.0	0.015	20.0	15.0	15.0	2.0	0.4	1.5
6	210	58	0.1	0.005	6.4	1.0	5.0	1.2	0.4	2.9
7	200	56	1.0	0.017	14.0	16.0	3.0	1.0	0.15	1.0
8	35	40	0.7	0.01	3.3	3.0	3.0	1.0	0.2	1.5
9	20	25	0.1	0.008	1.0	3.6	1.0	0.4	0.05	0.3
10	10	15	0.1	0.009	10.0	0.6	1.0	0.1	0.05	0.2
11	67	90	0.3	0.003	4.0	1.3	4.0	1.1	0.15	1.0
12	54	72	0.2	0.006	7.8	0.8	2.5	0.7	0.1	0.7
13	350	46	3.5	0.006	1.5	1.5	3.0	2.0	0.5	3.0
14	35	5	0.1	0.007	1.0	1.0	5.0	0.7	0.2	0.9
15	50	6	90	0.007	1.0	1.0	10.0	5.0	0.4	1.6
16	60	10	70	0.025	7.0	7.0	6.0	1.5	0.3	1.0

Chemism of Radiolarian Lydites from the Bohemian Massif Region



FIG. 7  
Distribution of Vanadium in the Sample No. 15, Zdechovice (Magnif. 1500 $\times$ )

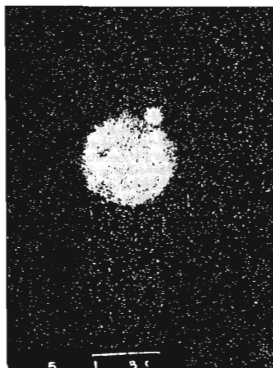


FIG. 8  
Distribution of Calcium in the Sample No. 3, Zálesí (Magnif. 1000 $\times$ )

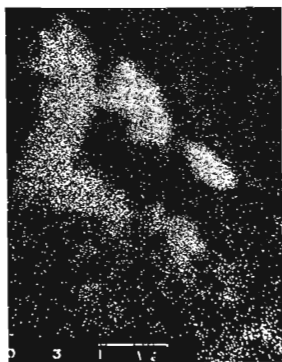


FIG. 9  
Distribution of Silver in the Sample No. 2, Borovy (Magnif. 250 $\times$ )



FIG. 10  
Distribution of Sulfur in the Sample No. 2, Borovy (Magnif. 250 $\times$ )



TABLE II

(continued)

SrO %	BaO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	P <sub>2</sub> O <sub>5</sub> %	S %	H <sub>2</sub> O <sup>+</sup> %	H <sub>2</sub> O <sup>-</sup> %	CO <sub>2</sub> %	C <sub>combust.</sub> %	Σ org. subst. ppm
0.002	0.01	0.002	0.05	0.015	0.016	0.13	0.07	0.01	0.79	1.18
0.01	0.01	0.04	0.05	0.02	0.42	0.15	0.04	0.55	0.62	1.33
0.0004	0.015	0.003	0.02	0.02	0.051	0.12	0.02	0.01	0.08	1.34
0.0005	0.006	0.003	0.02	0.007	0.04	0.06	0.03	0.01	0.62	1.30
0.01	0.065	0.006	0.1	0.06	0.11	0.23	0.03	0.01	0.026	0.29
0.01	0.04	0.002	0.02	0.03	0.12	0.1	0.02	0.01	0.03	0.30
0.001	0.02	0.007	0.1	0.015	0.032	0.16	0.04	0.01	0.15	0.42
0.002	0.02	0.01	0.08	0.022	0.16	0.21	0.05	0.01	0.03	0.66
0.001	0.01	0.002	0.04	0.007	0.06	0.06	0.05	0.01	0.52	0.55
0.001	0.01	0.004	0.07	0.006	0.12	0.15	0.01	0.01	0.03	0.51
0.002	0.005	0.004	0.02	0.012	0.22	0.18	0.1	0.01	0.95	5.00
0.001	0.01	0.003	0.05	0.009	0.18	0.16	0.05	0.01	0.67	2.84
0.001	0.01	0.008	0.04	0.05	0.21	0.33	0.04	0.01	2.08	1.37
0.001	0.004	0.004	0.11	0.002	0.013	0.06	0.01	0.01	0.34	1.12
0.002	0.008	0.02	0.75	0.10	0.02	3.35	0.1	0.01	0.034	1.15
0.004	0.08	0.04	0.95	0.027	0.007	2.42	0.07	0.01	0.035	1.16

TABLE III

(continued)

W ppm	Au ppm	Th ppm	U ppm	Cl ppm	I ppm	FeS <sub>2</sub> %	Σ admixts. %	spectrally found
0.3	—	1.20	1.9	18	0.1	0.03	1.77	Cr, B, Mo, Ag, Pb
0.01	9.0	0.80	3.0	4	0.1	0.79	3.89	{B, Cr, Zr, Co, Pb, Ag, Zn, Mo, Ni
0.5	4.9	1.63	15.0	14	0.3	0.09	1.60	{Cr, Ni, Zn, Ag, Co, Sn, B, Be, Pb
0.4	0.1	0.80	1.0	15	4.0	0.075	1.46	Cr
0.5	3.6	0.60	4.0	10	1.0	0.21	2.48	Cr, Ag
1.3	—	1.41	2.5	10	0.5	0.22	1.35	Cr
0.3	0.2	0.98	4.0	15	0.9	0.06	2.07	Cr, Ag
0.6	0.1	0.94	0.7	30	7.0	0.30	1.74	Cr
0.3	—	1.00	0.9	11	0.1	0.12	1.55	B, Cr, Ag
0.1	—	0.60	0.6	19	0.1	0.22	1.59	B, Zr
0.01	4.0	1.80	3.0	17	0.4	0.41	2.17	Cr, Ag
0.01	1.0	1.30	2.4	18	0.3	0.34	2.01	Cr, B, Zr, Ag
1.0	18.0	2.50	6.0	10	0.1	0.40	3.79	Cr, Zr, Ni, B, Pb, Ag
0.3	—	—	0.9	17	0.2	0.02	1.17	Cr, Ag
0.5	—	7.50	1.2	9	0.1	0.38	15.93	Cr, B, Ag
0.7	0.1	—	1.5	15	0.1	0.01	14.55	Li, Cr, Ag, Pb, Ni, B

TABLE IV

Results of Semiquantitative Spectral Analyses of the Lydites (Samples No 1—16)

Sample No.	Locality	Contents of elements determined		
		>10%	10—1%	1—0.1%
1	Malá Doubrava	Si		(Fe)
2	Borovy	Si	Fe, (Ca)	Na, Mg, Al, Ti, (K, Mn)
3	Zálesí	Si	(Fe)	(Al)
4	Vodokrty	Si		(Al)
5	Starý Plzenec	Si		Al, Fe
6	Starý Plzenec	Si		Al, Fe
7	Ostrá Hůrka	Si		Al, Fe
8	Kyšice	Si		Al, Fe
9	Ládví	Si		Al, Fe
10	Šárka	Si		Al
11	Šárka	Si		Al, Fe
12	Šárka	Si		Al, Fe
13	Mořičov	Si		Al, Fe
14	Sovolusky	Si		Al, Fe
15	Zdechovice	Si	Al	Mg, K, Ca, Ti
16	Zdechovice	Si	Al	K, Mg, Ti

metals (particularly potassium) and from electron microprobe observations, although they cannot be detected by X-rays, owing to their low concentrations.

We focused the study of composition of the lydites on the trace contents of those elements whose biogenic origin or enrichment can be assumed. These are particularly vanadium, copper and uranium, whose enhanced contents in sedimentary rocks, especially in the organic mass of the sediments, have been reported in papers of other authors<sup>20-24</sup>. The enrichment of vanadium and uranium by the organic mass occurs mainly in deep-sea sediments<sup>25</sup>, that of copper in freshwater and shelf sedimentary rocks<sup>26</sup>.

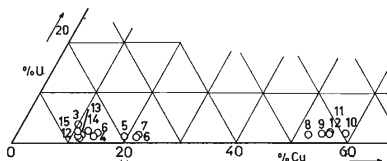


FIG. 3

Triangular Diagram (Section) for the Relative Contents of V, Cu, and U

TABLE IV  
(continued)

by semiquantitative spectral analysis

0.1–0.01%	0.01–0.001%	<0.001%
Al, (Mg, Ti)	V, Cr, (Mn, B)	Ca, Cu, Mo, Ag, Pb
V, Ba	B, Cr, Cu, Sr, Zr, Zn, (Ni, Ga, Mo)	Co, Ag, Pb
Mg, Ca, V	Cr, Mn, Ni, Cu, Zn, Sr, Ba, (Pb)	B, Co, Ag, Sn, (Be)
V, Fe, (Mg)	Ti, (Ca, Cr, Cu)	Mn
Mg	Ca, V, Cu, Ba, (Cr)	Ti, Mn, Ga, Sr, (Ag)
Mg, (Ca)	Ti, V, Cr, Cu, Ba, (Sr)	Mn, Ga
Mg, (Ca)	Ti, V, Cr, Cu, Ba	Mn, Ga, Sr, Ag
	Mg, Ca, Ti, V, Mn, Cu, Ba	Cr
	Mg, Ti, V, Cu, (Ca, Mn, Ag)	B, Cr
Fe	B, Mg, Ca, Ti, (Mn, Cu, Ba)	V, Zr
	V, Cu, (Ca)	Mg, Ti, Mn, Cr, (Ag)
	Mg, V, Cu, Cr, (Ca, Ti)	B, Mn, Zr, Ag, Ba
Mg, Ti, V	Ca, Cr, Cu, (Mn)	Ni, Ga, Mo, Ag, Ba, Pb
Mg	Ag, (Ti)	V, Cr, Cu
Fe	V, Cr, Mn, (Ag)	B, Cu, Ga
Na, Ca, Ba	Li, V, Cr, Cu, Sr, Ag	B, Ni, Ge, Pb

The contents of vanadium, copper, and uranium were plotted to give a triangular diagram (Fig. 3, Table VI); as can be seen from it, the lydites can be divided into two groups, principally according to the different V : Cu ratio. Two genetic groups

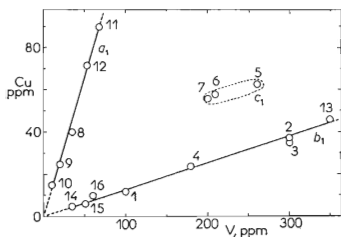


FIG. 4  
Interdependence of the Contents of Vanadium and Copper in the Lydites

Samples No. 1–16;  $a_1$ ,  $b_1$ ,  $c_1$  — genetic groups.

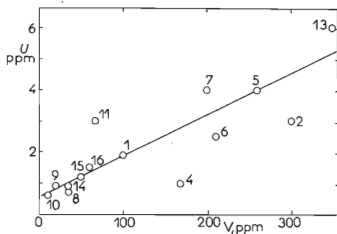


FIG. 5  
Interdependence of the Contents of Vanadium and Uranium in the Lydites

Samples No. 1–16.

TABLE V  
Survey of Chemical Analyses of Some Silicitic Rocks Reported in the Literature<sup>a</sup>

Sample No.	Locality rock	SiO <sub>2</sub> %	TiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	FeO %	MnO %	MgO %
1	Osterode (Harz) Kieselschiefer	61.24		18.75		11.70		4.91
2	Lerbach (Harz) Kieselschiefer	71.60		14.75	1.41		tr.	tr.
3	Andreasberg (Harz) Kieselschiefer	61.87		0.23		6.98		2.11
4	Australia black phthanite (radiolar.)	91.06		3.79	2.01			0.46
5	Borneo phthanite	97.19		1.45	1.12			tr.
6	Ireland chert	95.50		0.10	1.95	0.15		tr.
7	Belleville Missouri (USA) chert	98.17			0.83			0.01
8	Lande des Vardes (Normandy) phthanite (M. Armoricaïn)	97.85		1.08	0.87			tr.
9	Lamballe (Bretagne) phthanite (M. Armoricaïn)	98.00		1.22	0.23			tr.
10	The Vosges (France) radiolarite	86.84	0.38	6.03	0.10	2.62	0.04	0.67
11	Carnian Alps	91.55	0.23	2.85	0.20	0.54	tr.	0.37
12	Feistrichtzgraben lydite	95.11	tr.	0.46	0.42	0.03	0.01	0.14
13		95.94	tr.	1.39	0.69	0.05	0.01	0.26
14	Ohio (USA) flint ridge	98.93	0.005	0.14	0.06	0.08	0.01	0.02
15	Hengstrücken (Harz) lydite	90.42		3.24	1.58	0.63		0.28
16	Saratov region (USSR) hornstone (almost black)	97.16	0.08	0.20	0.12			0.40
17	South Ural phthanite	90.52	0.12	2.50	0.95		0.022	4.58
18	Lande des Vardes Manche, Normandy	95.50	0.07	2.10	0.65	0.70	tr.	0.30
19	Massif Armoricaïn phthanite	96.60	0.05	1.65	0.50	0.60	tr.	0.30
20		98.60	0.05	1.10	0.12	0.15	tr.	0.30
21	Hradiště W. of Prague lydite	97.94		1.37	0.18			0.06

TABLE V  
(continued)

CaO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	H <sub>2</sub> O %	C %	Σ %	Year	Ref.	Other components %
0.05	2.59	1.22		0.49	100.95	1 795	27	(cited on p. 346, the original paper not available)
1.06	10.06	0.32			99.20	1 866	27	traces of S and Mn
25.80	1.02	0.33		tr.	98.64	1 866	27	FeCO <sub>3</sub> 0.30
0.45	0.28		0.32		98.72	1 923	28	SO <sub>3</sub> 0.35
0.05		1.15	0.06		101.02	1 923	28	
	tr.				100.00	1 924	29	CaCO <sub>3</sub> 0.87, a.l. 1.43, CaSO <sub>4</sub> traces
0.5					98.84	1 924	29	a.l. 0.78
			0.10		99.90	1 929	30	
tr.			0.35		99.80	1 929	30	
0.42	0.49	1.32	1.38		100.69	1 933	31	H <sub>2</sub> O <sup>+</sup> 1.16, H <sub>2</sub> O <sup>-</sup> 0.22
0.00	0.24		0.21*	0.94	99.75	1 941	32	*H <sub>2</sub> O <sup>-</sup> , P <sub>2</sub> O <sub>5</sub> tr., CO <sub>2</sub> 0.0, a.l. 1.14, FeS <sub>2</sub> 0.32
0.00	0.06		0.16*	1.96	99.43	1 941	32	*H <sub>2</sub> O <sup>-</sup> , P <sub>2</sub> O <sub>5</sub> 0.01, CO <sub>2</sub> 0.0, a.l. 0.87, S tr.
0.00	0.13		0.06*	0.30	99.81	1 941	32	*H <sub>2</sub> O <sup>-</sup> , P <sub>2</sub> O <sub>5</sub> 0.02, CO <sub>2</sub> 0.0, a.l. 0.42, S tr.
0.04	0.01	0.01	0.44	0.18	99.92	1 949	33	CO <sub>2</sub> 0.02, P <sub>2</sub> O <sub>5</sub> 0.01, SO <sub>3</sub> tr., H <sub>2</sub> O <sup>+</sup> 0.17, H <sub>2</sub> O <sup>-</sup> 0.27
1.70	0.71	0.39	2.31	0.59	101.88	1 949	34	CuFeS <sub>2</sub> 0.01, Cl 0.03
1.00					98.96	1 953	35	
10.00				1.44	110.55	1 963	36	P <sub>2</sub> O <sub>5</sub> 0.42
tr.	tr.	0.25		0.45	100.47	1 971	18	a.l. 0.90, P <sub>2</sub> O <sub>5</sub> tr.
tr.	tr.	0.12		0.47	100.52	1 971	18	a.l. 0.70, P <sub>2</sub> O <sub>5</sub> tr.
tr.	tr.	0.08			100.75	1 971	18	a.l. 0.35, P <sub>2</sub> O <sub>5</sub> tr.
0.28			0.13		99.96	1 896	37	

TABLE V  
(continued)

Sample No.	Locality rock	SiO <sub>2</sub> %	TiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	FeO %	MnO %	MgO %
22	Špičaté skály W. of Prague lydite	97.86		1.44	0.20			0.07
23	Kámen near Nepomuky lydite	98.42		1.16	0.28			
24	Šárka, Džbán (Prague) lydite	97.91		1.35	0.18			0.04
25	Bohemian Massif region <sup>b</sup> lydites	94.16		0.82	1.65			
26		94.74		0.64	1.66	1.66		
27		95.05		1.44	0.97			
28		95.10		0.88	1.13			
29		95.30		0.99	1.19			
30		95.49		0.94	0.83			
31		95.16		0.95	1.27			
32	Bohemian Massif region <sup>c</sup> lydites	95-99	0-0.1	0.2-3 ∅ 1	0.1-3 ∅ 1			0-0.1

<sup>a</sup> Abbreviations used: tr. traces, a. 1. annealing losses; <sup>b</sup> closer specification of the localities not

of lydites with the content ratio V : Cu ~0.75 and ~7.7 are apparent also in the plots of Fig. 4; the V : U ratio is approximately constant in the rocks studied (V : U ~48), as follows also from the plot of Fig. 5.

From Fig. 4, two linear dependences (straight lines  $a_1$ ,  $b_1$ ) are apparent, which indicates that the content of vanadium increases with the increasing copper content; they divide the lydites into the two groups mentioned.

Isolated appears to be the group of samples denoted as  $c_1$  (Starý Plzenec, Ostrá Hůrka), where the rocks can be assumed to have been secondarily enriched by minerali-

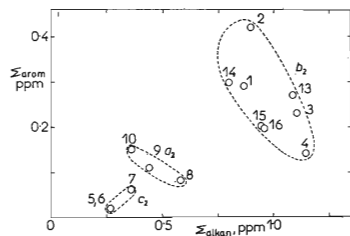


FIG. 6

Interdependence of the Contents of Alkanes and Aromatic Compounds in the Lydites as Determined by Means of Pyrolysis Gas Chromatography

Samples No. 1-10 and 13-16;  $a_2$ ,  $b_2$ ,  $c_2$  — genetic groups.

TABLE V  
 (continued)

CaO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	H <sub>2</sub> O %	C %	Σ %	Year	Ref.	Other components %
0.26			0.13		99.96	1 896	37	
			0.09		99.96	1 896	37	
0.29			0.13		99.90	1 896	37	
1.89					98.52	1 952	7	
1.86					98.90	1 952	7	
1.54					99.00	1 952	7	
1.31					98.42	1 952	7	
1.32					98.80	1 952	7	
1.56					98.92	1 952	7	
1.42					98.80	1 952	7	
0.1—0.4						1 954	8	
∅ 0.2								

reported; <sup>c</sup> average and limit values of 47 analyses, P<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub> detected only qualitatively.

zation processes of atmospheric waters, which leached the surrounding rocks, particularly the Barradien sedimentary iron ores. From the point of view of the dependences investigated, the samples No. 5–7 can be regarded as inappropriate for an explanation of the genetic problem of lydites based on the content of biogenic (proterozoic) relicts. This is supported also by the results depicted in Fig. 6; here the sum of the aromatic hydrocarbons is plotted against the sum of the alkane contents in the individual samples. Here, too, the samples divide into three groups (*a*<sub>2</sub>, *b*<sub>2</sub>, *c*<sub>2</sub>), which are virtually identical with the genetic groups expressed through other geochemical parameters (Fig. 4).<sup>\*</sup> Generally, increasing content of alkanes is accompanied by an increase of the content of aromatic hydrocarbons, which can be understood if the bitumens in the various samples are genetically related or even identical.

From the dependences, allowing for the geographic location of the localities of the groups of the lydite rocks in question, we can infer a very different depth of the proterozoic sea, where their sedimentation took place: the Middle Bohemia region represents a genetic complex corresponding to sedimentation in shallow

\* The high content of aromatics and alkanes in the samples No. 11 and 12 (Šárka) are not shown in the plot of Fig. 6; from the standpoint of the content of bitumenous substances these rocks are atypical.

sea, whereas the lydites and genetically related rocks from other localities display a deep sea nature as far as the vanadium and copper contents are concerned.

These results disagree with some theories concerning the circumstances of radiolarian sediment formation in Bohemia, and bring a new view upon the sedimentation cycles of formation of these rocks. Since the syngenetic age of the lydites in question could not be so far determined accurately enough by means of some of the radiometric geochronological methods, the two groups of lydite rocks mentioned may be associated with two different time periods of sedimentation, the sea depth (and hence the paleobiosphere) not being the determining factor for the different contents of the trace elements, especially as regards the V: Cu ratio. The different contents of some trace elements in the lydites can then result from the altered physico-chemical conditions of formation of these sediments and the different marinogenic biosphere occurring in the various periods of the proterozoic (paleozoic).

In order to specify the nature of the proterozoic biosphere, we examined the contents of organic substances in the radiolarian lydites. Gas chromatography was employed for the determination of the contents of the organic compounds whose elution times correspond to the hydrocarbons listed in Table VII. The column was chosen so as to enable separation of some typical aromatic compounds and determination of the sum of light hydrocarbons (up to C<sub>6</sub>) in the products of pyrolysis of bitumenous substances.

TABLE VI  
Relative Contents (Mutual Ratios) of V, Cu, and U in the Lydites (%)

Sample No.	Locality	V	Cu	U
1	Malá Doubrava	87-72	10-53	1-75
2	Borovy	88-24	10-88	0-88
3	Zálesí	85-71	10-00	4-29
4	Vodokrty	87-75	11-76	0-49
5	Starý Plzenec	79-51	19-27	1-22
6	Starý Plzenec	77-63	21-45	0-92
7	Ostrá Hůrka	76-92	21-54	1-54
8	Kyšice	46-23	52-85	0-92
9	Ládví	43-57	54-47	1-96
10	Šárka	39-22	58-82	1-96
11	Šárka	41-88	56-25	1-97
12	Šárka	42-06	56-07	1-87
13	Moříčov	87-06	11-44	1-50
14	Sovolusky	85-57	12-22	2-21
15	Zdechovice	87-41	10-49	2-10
16	Zdechovice	83-92	13-99	2-09



In the lydites, the contents of hydrocarbons up to  $C_5$  (methane predominates), n-hexane, and from aromatic compounds benzene, toluene, and xylenes were so determined. Other hydrocarbons, particularly those with a higher number of carbon atoms in the chain, are cracked or are present in low amounts, and therefore cannot be detected in this manner.\*

The total number of peaks in the chromatograms varied from 4 to 9, the total content of the organic substances determined lay in the range of 0.3 to 5 ppm.

The contents of the hydrocarbons found were compared with those of combustible carbon (Table VII); the results indicate only a negligible part of the hydrocarbons (and their derivatives, relicts of the biosphere) to remain preserved in this type of silicites, as follows from the high ratio of the contents of the combustible carbon and the hydrocarbons determined. The ratio (in mass %) ranges from  $3 \cdot 10^2$  to  $1.5 \cdot 10^4$ , in average  $3.3 \cdot 10^3$ . This gives evidence of an intense breakdown of the bitumenous substances, the metamorphism processes, however, not being strong enough to bring about a complete conversion of the organic substance as far as to graphite. In the separated carbonaceous component, obtained as the insoluble part after dissolving the sample in 10% hydrofluoric acid, graphite could not be reliably detected by the Debye-Scherrer technique; amorphous carbon is mostly present, with a low part of kerogene, graphite, and organic substances whose pyrolysis leads to the hydrocarbons determined (Table VII).

In the benzene extracts three hydrocarbons with 19 to 22 carbon atoms in the chain and eight hydrocarbons with 16 to 25 carbon atoms in the chain were found by mass spectrometry and gas chromatography. IR spectrometric analyses of an ethanolic extract of the organic substances present in the lydite from Šárka (sample No. 11) evidence the presence of carbonyl and carboxyl groups. The rather high pyrolysis temperature applied during the pyrolysis gas chromatography measurements does not allow hydrocarbons and their derivatives with so high-molecular a chain to be released from the sample without cracking; the pyrolysis gas chromatography results pertain therefore actually only to the breakdown products of more complex organic compounds.

#### *Distribution of the Trace Elements*

For a completion of the information on the composition of the lydite rocks, the spatial distribution of the various chemical elements in the lydite admixtures was determined by electron microprobe analysis. In addition to the common rock-forming elements

\* The values for the alkane and aromatics contents, as given in Table VII, mostly do not represent immediately the respective contents in the lydites, as they are due only to the products of pyrolysis of the bitumenous substances actually present in the rocks. In the original rock, much more complex organic substances may be present, as known from the compositions of bitumens.

TABLE VII  
Results of Pyrolysis Gas Chromatography Analyses of Bitumenous Substance

Sample No.	Locality	C <sub>compnst</sub> %	∑org. subst ppm	C <sub>1</sub> —C <sub>5</sub> ppm	C <sub>6</sub> ppm
1	Malá Doubrava	0.79	1.18	0.81	0.057
2	Borovy	0.62	1.33	0.84	0.06
3	Zálesí	0.08	1.34	1.06	0.05
4	Vodokrty	0.62	1.30	1.03	0.12
5	Starý Plzenec	0.026	0.29	0.25	0.02
6	Starý Plzenec	0.03	0.30	0.24	0.03
7	Ostrá Hůrka	0.15	0.42	0.30	0.06
8	Kyšice	0.03	0.66	0.45	0.13
9	Ládví	0.52	0.55	0.35	0.09
10	Šárka	0.03	0.51	0.31	0.05
11	Šárka	0.95	5.00	3.46	0.16
12	Šárka	0.67	2.84	1.97	0.08
13	Mořičov	2.08	1.37	0.74	0.35
14	Sovolusky	0.34	1.12	0.77	0.03
15	Zdechovice	0.034	1.15	0.81	0.14
16	Zdechovice	0.035	1.16	0.81	0.15

of aluminosilicate minerals (Mg, Al, Si, Ca, Na, K, Ti, Mn, Fe and others), other elements were determined by this technique too (V, P, S, C, Co, Ni, Cu, Ag, Au, U).

The photographs obtained from the electron microprobe measurements (Figs 7–10\*) show rather nonuniform distribution of the elements in the basic substance of the lydites – quartz. This holds for most of the elements followed, irrespective of whether they form accessory minerals, formed during the original sedimentation cycle, or whether they represent products of metamorphism processes or recent oxides of iron, *etc.* If the larger coatings of the secondary minerals are not taken into account, the elements examined form in the quartz mass of the lydites sites of higher concentrations with dimensions of the order of magnitude of 10–100 μm.

From the genetic aspect it is significant that some metals, whose biogenic origin can be assumed, are concentrated in centres of micrometer dimensions, which are rather nonuniformly scattered in the quartz mass. This applies first of all to vanadium (Fig. 9\*) and copper (and silver in some cases), but also to the distribution of some other elements such as titanium and sulfur (U, P, Co, Ni, Mg, and Na were not found by the microprobe technique). Similar findings pertaining to iron, manganese, calcium, and alkali metals are not of significance for a determination of genetic

\* See insert facing page 2306.

TABLE VII  
(continued)

$\Sigma$ Alkanes ppm	Benzene ppm	Toluene ppm	Xylenes ppm	$\Sigma$ Aromatics ppm	Nonidentd. hydrocarbons ppm	$C_{\text{combust.}} \cdot 10^3$ $\Sigma$ org. subst.
0.87	0.22	0.035	0.033	0.29	0.019	6.7
0.90	0.30	0.08	0.04	0.42	0.007	4.7
1.11	0.17	0.03	0.03	0.23	0.004	0.6
1.15	0.11	0.02	0.01	0.14	0.01	4.8
0.27	0.02	—	—	0.02	—	0.9
0.27	0.02	—	—	0.02	0.01	1.0
0.36	0.06	0.002	—	0.06	0.0004	3.6
0.58	0.07	0.005	—	0.08	0.002	0.5
0.44	0.09	0.02	0.001	0.11	—	9.5
0.36	0.13	0.02	—	0.15	0.004	0.6
3.62	1.17	0.04	0.15	1.36	0.02	1.9
2.05	0.65	0.03	0.08	0.76	0.03	2.4
1.09	0.24	0.02	0.01	0.27	0.01	15.2
0.80	0.27	0.03	0.001	0.30	0.02	3.0
0.95	0.02	0.16	0.02	0.20	0.004	0.3
0.96	0.02	0.15	0.02	0.19	0.007	0.3

dependences, as these elements form aluminosilicate rock-forming minerals, which are a common part of silicic rocks (clay minerals, feldspars, etc.).

The distribution of aluminium, potassium, and silicon in the sample No. 16 confirms the presence of clay minerals, detected also by X-ray analysis. The presence of feldspars is indicated *e.g.* by the aluminium, calcium, and potassium distributions (sample No. 6).

In addition to the crystalline grains of feldspars, amphiboles, micas, and other common aluminosilicate minerals appearing sporadically in some lydites, some other, prevalingly spherical or reniform formations, probably relicts of receptacles of the proterozoic marinogenic biosphere, were found by means of the microprobe (Fig. 8). A more detailed identification of the formations lies beyond the scope of this work.

In all the samples studied, sulfur was found to be absent from all the sites where vanadium and copper concentrate in higher amounts. Almost all the sulfidic sulfur\* is bound only to iron or silver (or other metals whose spatial distribution could not be

\* Virtually all the sulfur was found to be bound as sulfide or polysulfide (determined as combustible sulfur), sulfatic sulfur was not detected.

determined by the microprobe). From sulfides, virtually only pyrite is present\* (pyrrhotine was not detected chalcographically), argentite appears rarely in very fine aggregations (tenths of mm, Figs 9, 10).

As to the other elements followed by the microprobe, they could not be detected owing to their very low contents or to their highly homogeneous dispersion in the lydite mass; results of semiquantitative spectral analyses, however, confirm their presence — see Table IV.

*The authors wish to thank Academician V. Zoubek for interest devoted to this work.*

#### REFERENCES

1. Kettner R.: *Geol. Rdsch.*, VIII. 5/8, 169 (1917).
2. Kodym O.: *Geologické jednotky Českého masivu*. *Geol. Sbor.* 9, 2. Slov. Akad. Vied, Bratislava 1958.
3. Rodič I.: *Lotos* 79, 118 (1931).
4. Zoubek V.: *Sbor. Stát. Geol. Úst. ČSR* 15, 339 (1948).
5. Petránek J., Eliáš M., Kukul Z., Skoček V.: *Věstník Ústř. Úst. Geol.* 36, 6, 417 (1961).
6. Dubanská V.: *Thesis*. Czechoslovak Academy of Sciences, Prague, Ostrava 1974.
7. Bárta R., Vašíček J.: Unpublished results.
8. Bárta R., Vašíček J., Vepřek O.: *Hutn. Listy* 9, 11 (1954).
9. Konta J.: *Jilové minerály Československa*, p. 83. Academia, Prague 1957.
10. *Jednotné analytické metody*. Archives of the Geological Institute of Czechoslovak Academy of Sciences, Prague 1972.
11. Fráňa J., Maštalka A.: Proceedings of the Conference on Instrumental Activation Analysis (AA 73), Písek June 4—7, 1973, p. 30.
12. Podracký P.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1970.
13. Podracký P., Zeman J.: Unpublished results.
14. Dubanský A.: *Czech* 134 962, Prague 1970.
15. Dubanský A., Dubanská V.: Unpublished results.
16. Dubanská V., Dubanský A., Hejl V.: *Rudy* 23, 383 (1975).
17. Dubanská V., Dubanský A., Hejl V., Maštalka A.: *Rozpravy ČSAV*, in press.
18. Roblot M. M.: *Sci. de la Terre Mém. (Nancy)* 20, 9 (1971).
19. Mikheev V. I.: *Rentgenometricheskii Opredelitel Mineralov*, p. 387. Nauchno-Tekhn. Izd. Lit. Geol. i Okhr. Nedr., Moscow 1957.
20. Katchenkov S. M.: *Malye Khimicheskie Elementy v Osadochnykh Porodakh i Neftyakh*, p. 59. Gostoptekhizdat, Moscow 1959.
21. Manskaya S. M., Drozdova T. V.: *Geokhimiya Organicheskogo Veshchestva*, p. 167. Izd. Nauka, Moscow 1964.
22. Naumov G. B., Kochenov A. V., Gerasimovskii V. I., Germanov A. I.: *Uran v Osadochnykh Porodakh. Osnovnye Cherty Geokhimií Urana*. Izd. Nauka, Moscow 1963.
23. Füchtbauer H., Müller G.: *Sedimente und Sedimentgesteine*. Schweitzerbartsche Verlagsbuchhandlung, Stuttgart 1970.
24. Vinogradov A. P. in the book: *Sbornik Posvyashchennyi Akademiku V. I. Vernadskomu*, p. 145. Izd. Nauka, Moscow 1936.

\* The chalcopyrite described in the literature is probably of secondary origin, similarly as other ore minerals reported as mineral admixtures in the vicinity of hydrothermal deposits, etc.

25. Gulyaeva L. A.: Tr. Inst. Nefti Akad. Nauk SSSR 2, 73 (1952).
26. Holland H. D., Kulp L. L.: Geochim. Cosmochim. Acta 5, 197 (1954).
27. Zirkel F.: *Lehrbuch der Petrographie*, p. 283. Wien 1866.
28. Lapparent J.: Bull. Serv. Ct. Géol. Alsace Lorraine 1, 47 (1923).
29. Clarke F. W.: The Data of Geochemistry B 770, 551 (1924).
30. Cayeux L.: *Les Roches Sédimentaires de France: Roches Siliceuses. Mém. Explic. Carte Géol. Dét. Fr.*, Vol. 1, p. 358. Imprim. Nationale, Paris 1929).
31. Jérémie E.: Bull. Serv. Ct. Géol. Fr. 38, 190, 94 (1933).
32. Heritsch F., Heritsch H.: Mitt. Alpenländ. Geol. Ver., Geol. Ges. 34, 127 (1941).
33. Pettijohn F. J.: *Sedimentary Rocks*, Part 1, p. 525. Harper and Brothers, New York 1949.
34. Correns C. W.: *Einführung in die Mineralogie (Kristallographie und Petrologie)*. Vol. 1, p. 381. Springer, Berlin 1949.
35. Ruchin L. B.: *Bases de la Lithologie. Etude des Formations Sédimentaires*. Vol. 1, p. 76. Leningrad 1953.
36. Khvorova I. V., Zalmanzon E. S.: Litol. Polezn. Iskop. 1, 73 (1963).
37. Vaetter E.: Čas. Prům. Chem. 6, 187 (1896).

Translated by P. Adámek.