

## GEOCHEMISTRY OF FLYSCH SEDIMENTS AND ITS APPLICATION IN GEOLOGICAL INTERPRETATIONS

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**Abstract:** On the basis of very similar mineralogic-geochemical character of the sediments of the Subchert beds and the Menilite Formation of the Silesian and Ždánice units it is possible to state that the sediments of the Subchert beds which were in the past assigned to the Submenilite Formation belong to the Menilite Formation.

Results of the mineralogic-geochemical study of the Krosno beds of the Silesian unit and Ždánice-Hustopeče Formation of the Ždánice unit suggest that the source areas of the investigated sediments were similar and that the sediments originated from a single important source area. During the deposition of the Krosno beds and Ždánice-Hustopeče Formation, clastic material was not transported from the deeply eroded Bohemian Massif, but more probably it was supplied from the east – Magura zone area.

**Key words:** Western Carpathians, sediments, flysch, analytic and geochemical methods, geochemical correlations.

### Introduction

In recent years I carried out mineralogic-geochemical research of flysch sediments in the western part of the Czechoslovak Carpathians. Significant tectonic units of the Carpathian Flysch Belt – Silesian, Ždánice-Subsilesian and Pouzdřany ones have been characterized in detail as regards their petrographic-mineralogical and geochemical properties (determination of geochemical characteristics of rocks based on the study of major and trace element concentrations, determination of their distribution, correlation relationships and geochemical background values in rocks of individual lithostratigraphic members of the studied tectonic units with possible application of geochemical evaluation for their distinguishing and stratigraphic correlation; Adamová 1983, 1986, 1988; Adamová and Stráník 1984).

This work is aimed at the application of geochemical data interpretation by the study of sediments of the Subcherty beds of the Menilite Formation of the Silesian and Ždánice units (the question of the assignation of the Subcherty beds) and at geochemical correlation of sediments of the Krosno beds of the Silesian unit and Ždánice-Hustopeče Formation of the Ždánice unit.

### Research methodics

Chip samples for the study (1.5 to 4.0 kg depending on planned analyses) were continuously collected from superficial outcrops and deep drillholes. All the samples were

divided into individual lithostratigraphic sets on the basis of lithology, stratigraphy and type of sample collection. List of sampling sites is given in Adamová (1983, 1986).

### Analytic methods

All the samples were analysed at laboratories of Geologický průzkum n. p. (Geological Survey) Ostrava, plant Brno. Standard set of trace elements was terminated by X-ray fluorescent spectral analysis (by the apparatus Philips PW 1410 with a 3 kW generator) with the following sensitivity (in ppm): As (5), Ba (50), Co (5), Nb (5), Ni (5), Pb (5), Rb (5), S (100), Sb (3), Sr (10), TiO<sub>2</sub> (20), U (10), V (5), Y (5), Zn (5), Zr (5). Emission spectral analysis (spectrophotograph of the firm Zeiss, type PGS 2 with a plane screen) was employed to determine concentrations of Ag (0.66), B (9), Ga, Mo and Sn (1). Contents of Sm (1), La (1), Au (0.05), Ce (1), Yb (1), Lu (0.01), Th (1), Eu (0.1), Tb (1), Rb (10), Co (1), Hf (1), Sb (1) and U (3) were determined by the method of instrumental neutron activation analysis at laboratories of Geoindustria n. p. Prague (threshold of sensitivity in ppm). U, Th, Ra and K contents were determined by gamma-spectrometric analysis (laboratories of Geofyzika n. p. Brno) in selected samples from individual lithostratigraphic members of studied sediments. The threshold of sensitivity of this method is following: U – 1.2 ppm, Ra – 0.13 ppm (expressed in U equivalent concentration), Th – 0.4 ppm and K – 0.07 %.

Complete silicate analyses were carried out at laboratories of Ústřední ústav geologický (Central Geological Institute)

Prague and Geologický průzkum n. p. Ostrava, plant Brno. All analyses were carried out in the samples in their original state (without separation).

Mineralogical composition of selected samples was studied by means of X-ray diffraction analysis and was compared with the results of differential thermic analysis. Some samples were analysed in detail by means of diffraction phase analysis (Ústřední ústav geologický, Prague) which is based on the determination of the best correlation between measured diffraction data of a sample and theoretical diffractogram of mixture (Moravcová and Fiala 1980). Heavy minerals were analysed in selected samples of studied sediments (laboratories of Ústřední ústav geologický, Prague).

Organic matter was analysed at laboratories of Moravské naftové doly (Moravian Petroleum Mines), Hodonín by a standard method determining individual genetic types of organic substance in a decalcinated rock.

### *Geochemical methods*

Development of the chemical composition of flysch rocks is closely associated with the history of the geotectonic development of the geosynclinal area. Chemical composition of the sediments was controlled predominantly by the tectonic regime, composition of source areas and hydrodynamic regime of the basins. Complete recognition of the rock character requires the study of major chemical components of the rocks as well as study of concentrations, distributions and correlation relationships of trace elements supplemented by the research of their mineral composition and organic matter.

The principal classification criterion of statistical treatment was classifying of original data according to their assignation to a certain tectonic unit into individual lithostratigraphic populations. Basic statistical treatment within these populations was carried out in RVS Geoindustria n. p., Prague.

Average contents of evaluated elements thus obtained in the individual lithostratigraphic populations were:

a) compared to clark values of the corresponding lithological sediment type (Ronov et al. 1965; Wedepohl 1968; Kraft et al. 1969; Krauskopf 1967; Fairbridge 1972);

b) changes in element concentrations in individual lithostratigraphic members of the studied tectonic unit were observed;

c) data concerning sediments of the same lithostratigraphic position from the individual tectonic units were mutually compared.

In addition to the study of major and trace element concentrations, geochemical characteristics of rocks requires also comparison of ratios of selected pairs of studied elements and observation of changes in average values of these ratios between lithostratigraphic members of a tectonic unit or between individual tectonic units. For example,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in excess of 3 (Kukal 1962) indicates the share of clastic quartz or other  $\text{SiO}_2$  forms of more than 25 %, whereas  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  ratio (Pettijohn 1957) expresses chemical maturity of pelitic sediments (in chemically most mature sediments the ratio may reach 125).  $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}/\text{Na}_2\text{O} + \text{MgO}$ ,  $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ,  $\text{Rb}/\text{K}_2\text{O}$  ratios represent, according to Taylor (1965), Björklöf (1974 a, b) and Dipvik (1977), other indices of pelitic sediment maturity. Lower values of  $\Sigma \text{Fe}/\text{P}_2\text{O}_5$  ratio suggest possible enrichment of the sediment in phosphorus, e.g. of organic origin.  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio determined in fresh rocks from drillholes may be used to

characterize redox of the environment. Increased values of  $\text{Ti}/\text{Zr}$ ,  $\text{V}/\text{Zr}$ ,  $\text{Ni}/\text{Co}$ ,  $\text{Mn}/\text{V}$  and  $\text{V}/\text{Cu}$  indicate that mafic rocks were more significantly involved in the flysch sediment formation. On the other hand, prevailing high  $\text{Ti}/\text{Cr}$ ,  $\text{Cu}/\text{Ni}$ ,  $\text{V}/\text{Cr}$ ,  $\text{Zr}/\text{Ni}$  and  $\text{Zr}/\text{Cr}$  values suggest that also fragments of acid and intermediate rocks were deposited.

Increased  $\text{La}/\text{Th}$  values and low  $\text{Th}/\text{U}$  values indicate presence of volcanogene material in the sediment (Mc Lennan 1980; Bhatia and Taylor, 1981).

Pilger and Adams (1962) give the average  $\text{K}/\text{Th}$  value for pelitic sediments of 2200. Increased values of this ratio may, for example, reflect very rapid (even abrupt) sedimentation leaving little time for sorption of Th (Adamová 1986 – Godula formation of the Silesian unit).

Determination of the character of sedimentary environment, particularly salinity, is significant not only for the paleogeographic studies but also as an indirect method of stratigraphic correlation. Geochemical methods make it possible to distinguish only substantial differences in the salinity of sedimentary environment. It results from works dealing with these problems (Ernst and Werner 1964; Tourtelot 1964; Walker 1968; Cody 1970; Reynolds 1965, 1972; Bouška 1980; Adamová 1988b) that boron (and so-called equivalent boron – Reynolds 1965) and  $\text{Th}/\text{U}$  ratio (Adams and Weaver 1958) are especially suitable for the determination of the original salinity of a given environment.

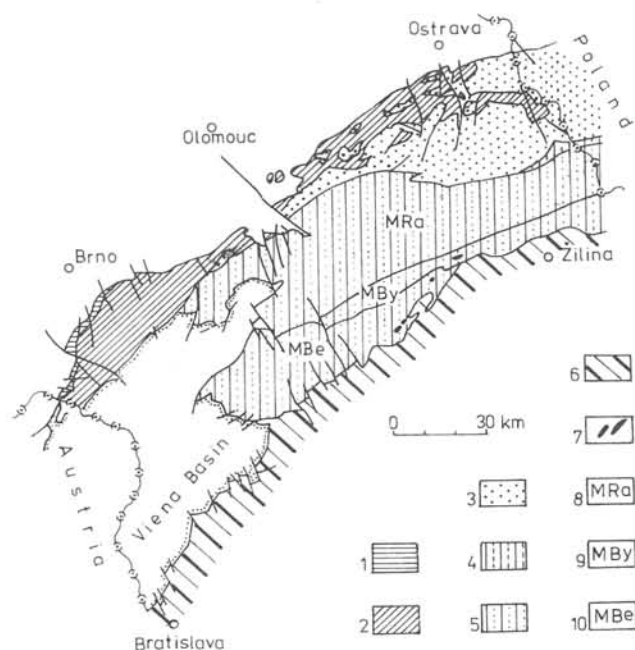
### **Geological characteristics**

The Carpathian Flysch Belt constitutes part of nappes (Inner Carpathian allochthon) which were folded and overthrust onto the original foreland of the Bohemian Massif and onto the Oligocene foredeep filling in the course of Savian and Styrian orogenic phases (Menčík et al. 1983). The Outer Carpathian Flysch Belt in Moravia and western Slovakia is divided into peripheral, central and Magura group. The Silesian and Ždánice-Subsilesian units comprise to the central group (Fig. 1).

In the Silesian unit, only its succession of strata of the Godula development (Upper Jurassic–Oligocene) was studied. Because of its areal extent, this development plays a decisive role in the structure of the Silesian unit in northern Moravia and is of prime importance for understanding the principal geochemical factors. In the Ždánice-Subsilesian unit, most attention was paid to the investigation of the Ždánice portion in which the sedimentary filling of the original geosynclinal area reached maximum thicknesses with a complete succession of strata from the Upper Cretaceous to Egerian.

The Submenilite Formation, the uppermost part of which is represented by the Globigerina Marls, is developed in the Silesian as well as Ždánice unit (its stratigraphic range in the Ždánice unit is Campanian–Lower Oligocene, in the Silesian unit it spans Paleocene–Upper Eocene). The Globigerina Marls are overlain by the so-called Subcherty beds until recently regarded as part of the Submenilite Formation.

An important correlation horizon in the Flysch Belt outer units is the Menilite Formation (Lower and Middle Oligocene) overlying the Subcherty beds. The formation consists of a lithologically varied sequence in which following beds can be distinguished from bottom to top: Cherty beds, Dynów Marlstones and in the Ždánice unit Šitbořice beds (Stráňík 1981; Brzobohatý and Stráňík 1981).



**Fig. 1.** Tectonic Flysch Units of the Moravian and West Slovakian region (Czechoslovakia).

1 – Pouzdrany unit; 2 – Ždánice-Subsilesian unit; 3 – Silesian unit; 4 – Fore-Magura unit; 5 – Magura flysch group; 6 – Mesozoic of the Klippen zone, Mesozoic of the Central Carpathians; 7 – Jurassic Klippes of the Pavlov Mts.; 8 – Račany unit; 9 – Bystrica unit; 10 – White Carpathians unit.

The youngest sediments of the Silesian unit are the Krosno beds (Oligocene), whereas in the Ždánice unit sedimentation represented by the Ždánice-Hustopeče Formation (Upper Oligocene–Lower Miocene) continued until the Miocene. The latter formation, which is areally the most extensive part of the Ždánice unit, is characterized by a great facies variability. Following developments have been distinguished within the formation: psammitic (so-called Ždánice Sandstones), psammitic-pelitic (flysch) and pelitic one (so-called Hustopeče Marls, Rzehak 1881). Laterally, the individual developments give way to one another. The Krosno beds in the Moravsko-Slezské Beskydy Mts. are present in incomplete thicknesses of less than 1000 metres and are characterized by alternating non-flysch and flysch, medium- to coarse-rhythmical sequence of gray calcareous claystones and thin- to thick-bedded micaceous calcareous sandstones.

#### Geochemical data interpretation by the study of sediments of the Subcherty beds and Menilite Formation of the Ždánice and Silesian units

##### *Petrographic-mineralogical characteristics*

Until recently the Subcherty beds were considered as the uppermost layer of the Submenilite Formation. They consist of brown variable-silty bedded noncalcareous as well as calcareous claystones, marlstones to clayey limestones. In addition to quartz, the minerals present include significant amounts of cristobalite which is always associated with zeolite (clinoptilolite) and montmorillonite. (Numerous authors:

Hay 1966; Reynolds 1970; Mizutani 1970; Hurd 1973, regard joint occurrence of these minerals in sediments as a result of alteration of fine-grained volcanic material). Some samples contain small amounts of mica minerals, exceptionally also kaolinite. Feldspar contents are low, amphibole, jarosite, gypsum and barite occur locally. Contents of carbonates, particularly those of calcite, are very variable – from traces to 65 %. Organic matter and pyrite are present in increased contents.

The Cherty beds of the Menilite Formation are represented by brown and black-gray variable-silicified noncalcareous and slightly calcareous claystones with intercalations and thin bands of light-gray diatomites and diatom claystones. In addition to quartz, mainly cristobalite and montmorillonite are present.  $\text{SiO}_2$  occurs also in the amorphous form as opal or chalcedony, in some samples tridymite was identified. Mica minerals are scarce or absent, kaolinite occurs even more rarely. Zeolite, jarosite, gypsum and barite were found in numerous samples. Contents of carbonates are low, with dolomite frequently predominating. Pyrite and organic matter contents are increased.

##### *Geochemical characteristics*

Rocks of the Cherty beds of the Menilite Formation and those of the Subcherty beds show highest  $\text{SiO}_2$  contents (Tab. 1) as well as highest  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (5.1 to 25) reflecting the intensity of their silicification, lowest  $\Sigma \text{Fe}$  contents (with  $\text{FeO}$  prevailing in drillhole samples), lower  $\text{Na}_2\text{O}$  contents and highest concentrations of  $\text{P}_2\text{O}_5$  (P is somewhat enriched relative to Fe, the enrichment being in good correlation also with the highest contents of organic matter suggesting that P is partly of organic origin). The studied sediments are characterized by the highest contents of As, Ba, S (sulphur is likely to be in part of organic origin), Mo, V and U (Tab. 2). Higher Mo and U contents may be, according to many authors, increased due to the presence of pyroclastic material. This fact well corresponds to a high Mo content, particularly in the Silesian unit tuffite (intercalations of tuffitic deposits in the Menilite Formation which consist of quartz, cristobalite, montmorillonite, in the Silesian unit the tuffites contain also chlorite, sometimes zeolite and traces of amphibole and feldspar). The tuffitic sediments contain the highest amounts of Mn, As, Ni, U, increased amount of Mo and in the Silesian unit mainly V. Biochemical concentration of Mo depends on the character of plankton prevailing in the sedimentary basin. According to Aron et al. (1955), molybdenum is a biocatalyzer significantly activating transformation of nitrates to nitrites in blue-green and green algae. Calcareous-plankton-dominated sediments contain higher Mo concentrations. Important hosts to V are clay minerals, mainly montmorillonite-group minerals and Fe-oxidic ones. Vanadium also tends to concentrate biochemically in sediments dominated by siliceous plankton where it acts as a catalyzer in the photosynthesis process (Harvey 1939; Aron and Wessels 1953). This element is preserved in sediments because it forms solid metalloorganic complexes. Increased V contents may occur in pyroclastic material (high content of vanadium in the Silesian unit tuffite – 1121 ppm). Increased Mo and V contents in the Subcherty beds and Menilite Formation correspond to a mixed character of plankton. The study results suggest that Mo and V in the investigated sediments concentrated both biochemically (high positive correlations with Mo, U, Cu, Ni and organic matter)

**Table 1.** Mean contents (m — median) of major element oxides (in %) and mean ratios of selected oxides of major elements in rocks of the Menilitic Formation, Krosno beds and Ždánice-Hustopeče Formation of the Silesian and Ždánice units (samples from outcrops).

a) *Silesian unit*

| Stratigraphic position and lithology | No. of samples     | SiO <sub>2</sub><br>m | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO  | MnO  | MgO  | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | CO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | H <sub>2</sub> O <sup>+</sup> | SiO <sub>2</sub>               | Al <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O               | K <sub>2</sub> O + Na <sub>2</sub> O | MgO                            | CaO                            | Σ Fe oxides                    | Σ Fe oxides                    |                                |                                |
|--------------------------------------|--------------------|-----------------------|--------------------------------|--------------------------------|------|------|------|-------|-------------------|------------------|-----------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
|                                      |                    |                       |                                |                                |      |      |      |       |                   |                  |                 |                               |                               | Al <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O              | Al <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub>       | Al <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> |
| Krosno beds claystones               | 10                 | 45.0                  | 12.9                           | 1.5                            | 3.0  | 0.07 | 4.0  | 10.9  | 0.8               | 2.5              | 10.1            | 0.15                          | 4.4                           | 3.5                            | 18.6                           | 3.6                            | 0.26                                 | 0.32                           | 0.9                            | 0.38                           | 34.0                           |                                |                                |
|                                      | Mentlitz Formation | cherts                | 1                              | 80.2                           | 4.1  | 2.17 | 0.35 | 0.53  | 0.81              | 0.1              | 0.65            | 0.15                          | 0.49                          | 11.4                           | 19.9                           | 40.3                           | 6.5                                  | 0.19                           | 0.13                           | 0.2                            | 0.65                           | 5.2                            |                                |
|                                      |                    | claystones            | 12                             | 55.1                           | 13.4 | 1.9  | 2.8  | 0.04  | 1.4               | 4.1              | 0.5             | 2.3                           | 3.1                           | 0.30                           | 7.1                            | 4.8                            | 40.2                                 | 6.2                            | 0.11                           | 0.4                            | 0.41                           | 29.0                           |                                |
| Subcherty beds marlstone             | 1                  | 21.05                 | 7.6                            | 2.0                            | 0.62 | 0.06 | 0.70 | 30.03 | 0.04              | 1.03             | 24.33           | 0.16                          | 6.0                           | 2.7                            | 190                            | 25.8                           | 0.14                                 | 0.09                           | 4.0                            | 0.34                           | 16.4                           |                                |                                |

b) *Ždánice unit*

|                             |                                 |    |      |      |     |      |      |      |      |      |      |      |      |      |      |      |     |      |      |      |      |      |  |  |  |  |
|-----------------------------|---------------------------------|----|------|------|-----|------|------|------|------|------|------|------|------|------|------|------|-----|------|------|------|------|------|--|--|--|--|
| Ždánice-Hustopeče Formation | flysch development, claystones  | 11 | 50.0 | 12.4 | 2.8 | 1.4  | 0.06 | 4.4  | 11.1 | 0.9  | 2.5  | 10.1 | 0.16 | 4.0  | 4.1  | 15.7 | 3.0 | 0.27 | 0.36 | 0.94 | 0.34 | 28.5 |  |  |  |  |
|                             | pelitic development, claystones | 9  | 48.2 | 11.6 | 2.8 | 1.3  | 0.06 | 4.8  | 11.7 | 0.9  | 2.1  | 11.9 | 0.12 | 3.6  | 4.1  | 13.9 | 2.6 | 0.26 | 0.41 | 1.04 | 0.37 | 38.4 |  |  |  |  |
| Menilitic Formation         | silicities                      | 7  | 81.1 | 4.8  | 1.4 | 0.6  | 0.04 | 0.55 | 0.6  | 0.2  | 0.7  | 0.3  | 0.12 | 4.2  | 25.1 | 24.1 | 3.4 | 0.21 | 0.10 | 0.19 | 0.39 | 16.2 |  |  |  |  |
|                             | claystones                      | 14 | 73.1 | 10.0 | 3.0 | 0.3  | 0.01 | 1.0  | 1.2  | 0.2  | 1.3  | 0.5  | 0.33 | 4.9  | 10.8 | 53.3 | 6.4 | 0.17 | 0.11 | 0.16 | 0.35 | 15.3 |  |  |  |  |
|                             | tuffite                         | 1  | 68.8 | 15.3 | 3.3 | 0.16 | 2.02 | 1.04 | 1.71 | 0.17 | 0.49 | 0.57 | 0.25 | 6.95 | 4.5  | 89.8 | 2.9 | 0.04 | 0.07 | 0.11 | 0.23 | 13.8 |  |  |  |  |
|                             | claystones                      | 4  | 64.1 | 10.3 | 3.4 | 0.2  | 0.03 | 1.2  | 6.7  | 0.3  | 1.3  | 5.1  | 0.22 | 6.5  | 7.5  | 34.8 | 5.0 | 0.17 | 0.12 | 0.62 | 0.38 | 18.0 |  |  |  |  |
| Subcherty beds              | marlstones                      | 3  | 21.0 | 6.7  | 3.4 | 0.2  | 0.08 | 0.8  | 35.0 | 0.2  | 0.9  | 27.1 | 0.24 | 2.9  | 3.0  | 39.0 | 5.2 | 0.16 | 0.12 | 5.5  | 0.55 | 20.5 |  |  |  |  |

Σ Fe oxides is expressed as Fe<sub>2</sub>O<sub>3</sub>

**Table 2.** Mean contents ( $\bar{x}$  in populations of less than 25 samples — m) of studied trace elements (in ppm) in rocks of the Menilite Formation, Krosno beds and Źdánice-Hustopecze Formation of the Silesian and Źdánice units (samples from outcrops).

a) *Silesian unit*

| Stratigraphic position and lithology |                          | No. of samples | Ag<br>$\bar{x}$ (m) | As   | B   | Be  | Ba  | Co  | Cr  | Cu | Ga   | Mo   | Nb   | Ni | Pb  | Rb  | S      | Sb  | Sn  | Sr    | Th   | U    |
|--------------------------------------|--------------------------|----------------|---------------------|------|-----|-----|-----|-----|-----|----|------|------|------|----|-----|-----|--------|-----|-----|-------|------|------|
| Menilite Formation                   | Krosno beds — claystones | 27             | 0.14                | 11.3 | 78  | 2.3 | 365 | 14  | 100 | 40 | 13.5 | 6.1  | 9.8  | 61 | 21  | 112 | 6 940  | 1.9 | 1.9 | 210   | 9.2  | 4.2  |
|                                      | Cherty beds              | 1              | < 0.06              | 18.0 | 32  | —   | 269 | < 5 | 34  | 36 | 5.0  | 15.0 | < 5  | 18 | < 5 | 21  | 3 800  | < 1 | < 1 | 85    | 3.1  | 2.1  |
|                                      | claystones               | 25             | 0.2                 | 22.0 | 92  | 6.5 | 360 | 15  | 120 | 61 | 22.6 | 24.4 | 14.3 | 71 | 23  | 120 | 11 128 | 1.5 | 3.8 | 158   | 8.4  | 10.6 |
|                                      | tuffite                  | 1              | < 0.06              | 24   | 31  | —   | 529 | 26  | 110 | 43 | 13.0 | 20   | 9    | 80 | 22  | 42  | 8 100  | 2.7 | < 1 | 233   | 6.3  | 21.4 |
| Menilite Formation                   | Subcherty beds claystone | 1              | < 0.06              | 12   | 106 | —   | 339 | 22  | 122 | 94 | 26   | 7    | 14.0 | 69 | 30  | 94  | 17 000 | 2   | 1   | 209   | 11.5 | 10.2 |
|                                      | marlstone                | 1              | < 0.06              | 9    | 60  | —   | 219 | 5   | 60  | 59 | 2    | 2    | 9.0  | 57 | 6   | 41  | 8 800  | < 1 | < 1 | 1 000 | 3.5  | 4.7  |

b) *Źdánice unit*

|                              |                                  |    |        |       |       |     |         |      |       |       |      |      |      |         |    |       |           |     |       |       |         |           |
|------------------------------|----------------------------------|----|--------|-------|-------|-----|---------|------|-------|-------|------|------|------|---------|----|-------|-----------|-----|-------|-------|---------|-----------|
| Źdánice-Hustopecze Formation | flysch development — claystones  | 26 | 0.1    | 7.6   | 71    | 4.8 | 316     | 10   | 104   | 30    | 9.7  | 3.5  | 10.6 | 44      | 20 | 108   | 499       | 1.3 | 1.6   | 188   | 9.0     | 2.9       |
|                              | pelitic development — claystones | 25 | 0.1    | 4.0   | 97    | 2.4 | 312     | 8    | 110   | 27    | 13.3 | 3.0  | 9.6  | 34      | 17 | 101   | 274       | 3.8 | 1.6   | 242   | 7.0     | 2.4       |
|                              | silicites                        | 18 | 0.07   | 4.6   | 28    | 1.1 | 241     | 5.0  | 27    | 23    | 1.3  | 3.5  | 4.2  | 10      | 6  | 19    | 795       | 2.7 | 2.0   | 94    | 2.4     | 5.8       |
|                              | claystones                       | 23 | 0.12   | 10.0  | 74    | 1.2 | 452     | 10   | 72    | 58    | 7.8  | 16.5 | 9.1  | 34      | 15 | 55    | 2 451     | 2.3 | < 2.3 | 148   | 5.9     | 7.3       |
| Menilite Formation           | Cherty beds                      | 2  | < 0.06 | 34—47 | 35—58 | 3.0 | 158—186 | 5—15 | 30—36 | 50—69 | 4—5  | 5    | 8—10 | 108—110 | 5  | 20—25 | < 100—200 | 1—8 | < 1—3 | 22—85 | 5.0—6.2 | 21.4—26.2 |
|                              | tuffites                         | 13 | 0.07   | 23.0  | 45    | 1.9 | 1010    | 14   | 76    | 69    | 10.7 | 16.0 | 8.0  | 83      | 11 | 51    | 678       | 3.0 | 1.1   | 852   | 5.0     | 10.2      |
|                              | claystones                       | 3  | < 0.06 | 16.7  | 48    | 1.3 | 267     | 10   | 80    | 52    | 5.7  | 20.3 | 5.0  | 69      | 14 | 32    | 533       | 3.3 | < 1   | 1 179 | 5.1     | 9.8       |



Mean ratios of selected pairs of trace elements

a) *Silesian unit*

Continuation of Tab. 2

| Stratigraphic position and lithology  | No. of samples | Ti<br>$\bar{x}$ (m) | V    | Y  | Zn  | Zr  | B eq. | B/Ga | Sr/Ba | Ni/Co | Ti/Zr | V/Zr | V/Ni | V/Cu | V/Cr | Cr/Ni | Ti/Cr | Cu/Ni | Zr/Ni | Zr/Cr | Ga/V |
|---------------------------------------|----------------|---------------------|------|----|-----|-----|-------|------|-------|-------|-------|------|------|------|------|-------|-------|-------|-------|-------|------|
| Krosno beds claystones                | 27             | 3310                | 183  | 25 | 93  | 135 | 301   | 11.5 | 0.6   | 5.6   | 25    | 1.4  | 3.2  | 5.5  | 1.8  | 1.8   | 35    | 0.7   | 2.9   | 1.4   | 0.07 |
| cherts                                | 1              | 1439                | 92   | 7  | 19  | 25  | 592   | 6.4  | 0.3   | 9.0   | 58    | 3.7  | 5.1  | 2.6  | 2.7  | 1.9   | 42    | 2.0   | 1.4   | 0.7   | 0.05 |
| claystones                            | 25             | 4615                | 310  | 24 | 91  | 174 | 371   | 5.6  | 0.4   | 5.2   | 29    | 1.9  | 5.2  | 5.4  | 2.7  | 1.9   | 39    | 0.9   | 2.5   | 1.4   | 0.08 |
| tuffite                               | 1              | 3777                | 1121 | 14 | 105 | 80  | —     | 2.4  | 0.4   | 3.0   | 47    | 14.0 | 14.0 | 26.0 | 10.2 | 1.4   | 34    | 0.5   | 1.0   | 0.7   | 0.01 |
| Subcherty beds, claystones marlstones | 1              | 4436                | 247  | 26 | 102 | 150 | 448   | 4.1  | 0.6   | 3.1   | 30    | 1.6  | 3.6  | 2.6  | 2.0  | 1.8   | 36    | 1.3   | 2.1   | 1.2   | 0.09 |
|                                       | 1              | 1829                | 204  | 18 | 53  | 28  | 370   | 18.0 | 4.5   | 11.4  | 65    | 7.3  | 3.6  | 3.5  | 3.4  | 1.1   | 31    | 1.0   | 0.5   | 0.5   | 0.01 |

b) *Ždánice unit*

|                                   |                                    |    |               |             |           |             |             |             |              |             |              |           |             |      |             |             |     |           |             |             |     |      |
|-----------------------------------|------------------------------------|----|---------------|-------------|-----------|-------------|-------------|-------------|--------------|-------------|--------------|-----------|-------------|------|-------------|-------------|-----|-----------|-------------|-------------|-----|------|
| Zdánice-<br>Husopéce<br>Formation | flysch development<br>-claystones  | 26 | 3225          | 178         | 20        | 89          | 127         | 196         | 8.5          | 0.6         | 5.1          | 28        | 1.6         | 4.3  | 6.0         | 1.7         | 2.4 | 32        | 0.7         | 2.9         | 1.3 | 0.06 |
|                                   | pelitic development<br>-claystones | 25 | 2982          | 158         | 25        | 88          | 101         | 251         | 11.0         | 0.8         | 6.3          | 30        | 1.7         | 3.7  | 6.4         | 1.5         | 2.5 | 29        | 0.6         | 2.3         | 1.0 | 0.08 |
| Menilitic Formation               | silicites                          | 18 | 1091          | 76          | 9         | 21          | 20          | 408         | 18.2         | 0.6         | 2.4          | 53        | 4.6         | 18.0 | 3.4         | 2.5         | 2.9 | 36        | 2.9         | 4.6         | 0.7 | 0.03 |
|                                   | claystones                         | 23 | 2497          | 220         | 17        | 55          | 73          | 548         | 8.6          | 0.4         | 3.4          | 41        | 3.1         | 13.0 | 3.7         | 2.5         | 4.2 | 35        | 2.5         | 3.1         | 0.9 | 0.04 |
|                                   | tuffites                           | 2  | 2639—<br>2758 | 108—<br>113 | 11—<br>16 | 145—<br>164 | 101—<br>121 | 241—<br>911 | 7.0—<br>14.5 | 0.2—<br>0.5 | 7.3—<br>21.6 | 22—<br>27 | 1.0—<br>1.1 | 1.0  | 1.6—<br>2.2 | 3.1—<br>3.6 | 0.3 | 73—<br>92 | 0.5—<br>0.6 | 1.0—<br>1.1 | 3.3 | 0.04 |
| Subcherty<br>beds                 | claystones                         | 13 | 2284          | 298         | 22        | 78          | 47          | 402         | 5.8          | 1.1         | 5.6          | 48        | 6.3         | 3.2  | 4.5         | 3.7         | 1.0 | 29        | 0.8         | 0.6         | 0.5 | 0.04 |
|                                   | marlstones                         | 3  | 1700          | 312         | 17        | 53          | 38          | 378         | 8.2          | 4.7         | 7.8          | 45        | 8.2         | 4.2  | 5.7         | 3.8         | 1.1 | 22        | 0.7         | 0.5         | 0.5 | 0.02 |



as well as from pyroclastic material which was a primary source of at least part of these two elements. Uranium in the investigated sediments is probably of syngenetic origin and concentrates by sorption on planktonic organisms or organic substance during its bitumenization. The highest contents were observed in diatomites with fairly bitumen-rich organic substance. Transport of uranium associated with pyroclastic material into the basin of deposition is suggested by the increased content of this element in tuffitic sediments of the Menilite Formation of the Silesian as well as Ždánice units.

Ti, Y and rare earth (REE) contents (Tab. 3) in the Subcherty and Cherty beds of the Menilite Formation are relatively low, the sediments being characterized by the highest values of La/Th ratio (Tab. 3) and lowest ones of Th/U ratio. The same character was observed in the tuffitic material (increased La/Th and low Th/U values indicate presence of a material of volcanogene origin – Bhatia and Taylor 1981; Mc Lennan et al. 1981). High contents of organic matter, pyrite, generally low contents of total Fe dominated by FeO, similar concentrations of B and B equivalent values suggest clearly reducing character of the sedimentary environment of the Subcherty beds and Menilite Formation (particularly of the Cherty beds) only slightly communicating with the open sea and with normal to slightly increased salinity. Low Ti, Rb, Zr, Cr and Fe contents indicate minimum transport of clastic material.

#### **Geochemical correlation between the Krosno beds of the Silesian unit and Ždánice-Hustopeče Formation of the Ždánice unit**

##### *Petrographic, mineralogical characteristics*

The Krosno beds, gray variable-sandy calcareous claystones and marlstones are mineralogically characterized by quartz contents ranging from 25 to 30 % and higher proportion of feldspars amounting up to 15 %. Mica minerals (illite group and fine mica) which amount to 22 to 35 % are always accompanied by chlorite (up to 9 %), kaolinite occurs only sporadically and in small amounts, minerals of montmorillonite group were not found. Carbonates are dominated by calcite (up to 30 %), dolomite is abundant but variably distributed (up to 16 %). Overwhelming majority of samples contain pyrite (traces to 1 %). Heavy-mineral fraction comprises significant amounts of garnet, andalusite, cyanite and topaz.

The Ždánice-Hustopeče Formation. The pelitic facies is represented by gray variable-sandy yellow-green-weathering claystones. Intercalations and layers of brown-gray variable-calcareous claystones occur in places. The claystones contain laminae and rarely also thin benches of gray calcareous light-mica siltstones and fine-grained sandstones. Carbonate proportion in the studied claystones is very variable, ranging from several per cent to a maximum of 30 %. In addition to calcite the formation contains significant quantities of dolomite. Contents of quartz most frequently vary from 20 to 25 %, those of feldspar amount to approximately 9 %, only rarely exceeding 10 %. Clay fraction is dominated by mica minerals (about 25 %), chlorite is present in all samples in small to moderate quantities and so do montmorillonite-group minerals. Kaolinite occurs only exceptionally in very small amounts. Claystones often contain pyrite, locally also organic substance (predominantly in the basal part of the

formation). The psammitic-pelitic facies (flysch development) is characterized by rhythmically alternating claystones and sandstones of the same petrographic character as those in the pelitic facies. From the mineralogical point of view, claystones of the psammitic-pelitic facies are almost identical with claystones of the pelitic one. Some differences can be observed only in the quantitative presence of some minerals – slightly increased contents of quartz, feldspars and chlorite, with kaolinite and pyrite being present only in trace amounts in claystones of flysch development. Heavy-mineral fraction is dominated by garnet.

##### *Geochemical evaluation*

Sediments of the Krosno beds of the Silesian unit and those of the Ždánice-Hustopeče Formation of the Ždánice unit were compared on the basis of all data available. We may state that the sediments of both compared lithostratigraphic members are very similar in their mineral composition – higher contents of feldspars, dominant assemblages of mica minerals and chlorite-group minerals, significant share of dolomite in the carbonate admixture, heavy mineral fraction dominated by garnet. The sediments are characterized by their chemical immaturity. From the chemical point of view, they have very similar contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , iron oxides, MgO, CaO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{H}_2\text{O}^+$ , vast majority of trace elements (As, Co, Cu, Mo, Ni, S and U concentrations are slightly higher in the Silesian unit), similar average values of ratios of selected pairs of trace elements and absolute B contents. Rare-earth concentrations in the Krosno beds are only slightly higher, with the ratios of light and heavy rare-earth elements being identical. Th/U, La/Th, La/Ce, Th/Yb and K/Th ratios are also very similar (Tabs. 1, 2, 3). It results from this comparison that the source areas of sediments of the Ždánice-Hustopeče Formation and Krosno beds were similar or that they both originated in the same significant source area.

#### **Conclusions**

Very similar mineralogic-geochemical character of sediments of the Subcherty beds and Menilite Formation (mainly of the Cherty beds) of the Silesian and Ždánice units, i. e. identical mineral assemblages, clearly increased contents of organic matter, pyrite and similar concentrations of a number of major and trace elements, similar ratios of selected pairs of trace elements and La/Th, Th/U, Th/Yb, K/Th ratios, highest values of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, considerably similar correlations and distribution types of numerous elements make it possible to state that the sediments of the Subcherty beds, which were in the past assigned to the Submenilite Formation, should in fact belong into the Menilite Formation.

Results of the mineralogic-geochemical study of the Krosno beds of the Silesian unit and Ždánice-Hustopeče Formation of the Ždánice unit (very similar mineral composition, very similar contents of oxides of major elements and of overwhelming majority of trace elements, absolute boron contents, similar ratios of selected pairs of trace elements,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ , Th/U, La/Ce, Th/Yb and K/Th ratios) suggest that the source areas of the investigated sediments were similar or that the sediments originated from a single important source area. Significant presence of garnet



(sometimes also andalusite, cyanite and topaz) in the heavy-mineral fraction as well as lower Zr and Ti contents indicate that these sediments included also material from metamorphic rocks. During the deposition of the Krosno beds and Ždánice-Hustopeče Formation, clastic material (in contrast to older underlying sediments) was not transported from the deeply eroded Bohemian Massif but is likely to have come from the east, from the Magura zone area.

Translated by L. Böhmer

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