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Izabela BOJAKOWSKA, Jerzy BORUCKI

Molybdenum in stream sediment on the area of occurrence of the Dukla Folds and their margin

Molybdenum content in stream sediment in the western part of the Bieszczady Mts., eastern part of the Beskid Niski Mts. and southern margin of the Doły Jasielsko-Sanockie is contained from 0.1 up to 22.1 ppm and its average content amounts 1.25 ppm. Some zones of increasing molybdenum content in stream sediment have been fixed on geochemical maps in the area; they are orientated in the NW–SE direction. Comparison of the geological map and the geochemical maps of molybdenum content shows relation of the areas of higher molybdenum concentration in recent stream sediment to the areas of occurrence of Menilite Beds.

INTRODUCTION

Geochemical research of recent stream sediment have been used in maping for prospection of mineral resources for a few dozens of years (C. R. Butt, L. Nichol, 1979; G. D. Robinson, 1981). Geochemical mapping is also used more and more often in research of natural environment under anthropological impact during the last years (J. Lis, 1992).

Trace elements used to be mobilized on the Earth surface in the result of hypergenic geological processes and human economic activity. They penetrate to surface water together with surface discharge waters and sewages. Some parts of the substances present in water is deposited in the different kind of drainage system sediments. This is the result of (1) precipitation and sedimentation of insoluble substances and (2) adsorption by the sediment components, i.e. iron hydroxides, clay minerals and organic matter. In areas non-impacted by industrial pollution, chemical composition of stream water controls composition of sediments. Chemical composition of water is related to composition of soils and rocks of a catchment area. In strongly industrialized areas, composition of sewage supplying to surface water controls element concentration in stream sediment.

Heavy metals concentrations in stream sediment may be a good geochemical indicator and it makes possible to detect both the types of anomalies: (1) related to mineral resources ones and (2) anthropogenic ones, being the result of surface water pollution as a consequence of human technological activity.

"Regional geochemical survey of the Carpathian Mts." (I. Bojakowska et al., 1989) was made in the Polish Geological Institute during the period 1984–1989. The exploration covered area of 1700 km^2 in the river basins of Wetlina, Solinka, Osława, Wisłok and Jasiołka. Content of many elements, a.o. molybdenum, has been analysed in samples of active stream sediment.

EXPLORATION RANGE AND METHODS

Geochemical investigations covered the western part of the Bieszczady Mts., eastern part of the Beskid Niski Mts. and southern margin of the Doły Jasielsko-Sanockie.

State boundary between Ożenna village (placed to SW of Zyndramowa village) and the Szypowate Hill to SE from Wetlina village was the SE border of the investigated area. The line Baligród —Bukowsko — Iwonicz was the NW border of it. Meridians 21°40' and 22°31' were the west and east borders of the studied area. This area has been about 80 km long and 8–30 km wide being elongated towards NW–SE .

The geochemical survey covered almost the whole area of the Dukla Folds (Marginal Fold, Komańcza — Wisłok Wielki Slice, Pasieka Fold, Wysoki Groń Anticline) and the southern fragment of the Silesian Nappe (Bukowica Fold, Bystre Slice, Bóbrka — Rogi — Klimówka Anticline, Iwonicz — Rymanów — Baligród Anticline) — A. Ślączka, (1971), A. Ślączka, K. Żytko (1979).

Research groups of the Geophysical Research Enterprise in Warsaw accomplished field works during the period 1984–1987. Sampling density amounted 4 points for 1 km^2. 5252 samples of stream sediment have been taken in the studied area in creek heads, above potential pollution sources. The air-dry samples were crumbled and sieved with nylon screen. Fraction < 0.2 mm in diametre was used to analysis.

Determinations of molybdenum were made in the laboratory of the Institute of Nuclear Chemistry and Technology. Samples were extracted in a mixture of concentrated hydrochloric, nitric and perchloric acid. Molybdenum was atomized in a HGA graphite tube and the AAS measurements were made using a *Pye–Unicam SP–9–800* spectrometer.

RESULTS OF RESEARCH

STATISTICAL DISTRIBUTION OF MOLYBDENUM

Average molybdenum content in stream sediment of the studied area amounts to 1.25 ppm, median value 1.1, and the range from 0.1 (limit of the method sensitivity) to 22.1 ppm.

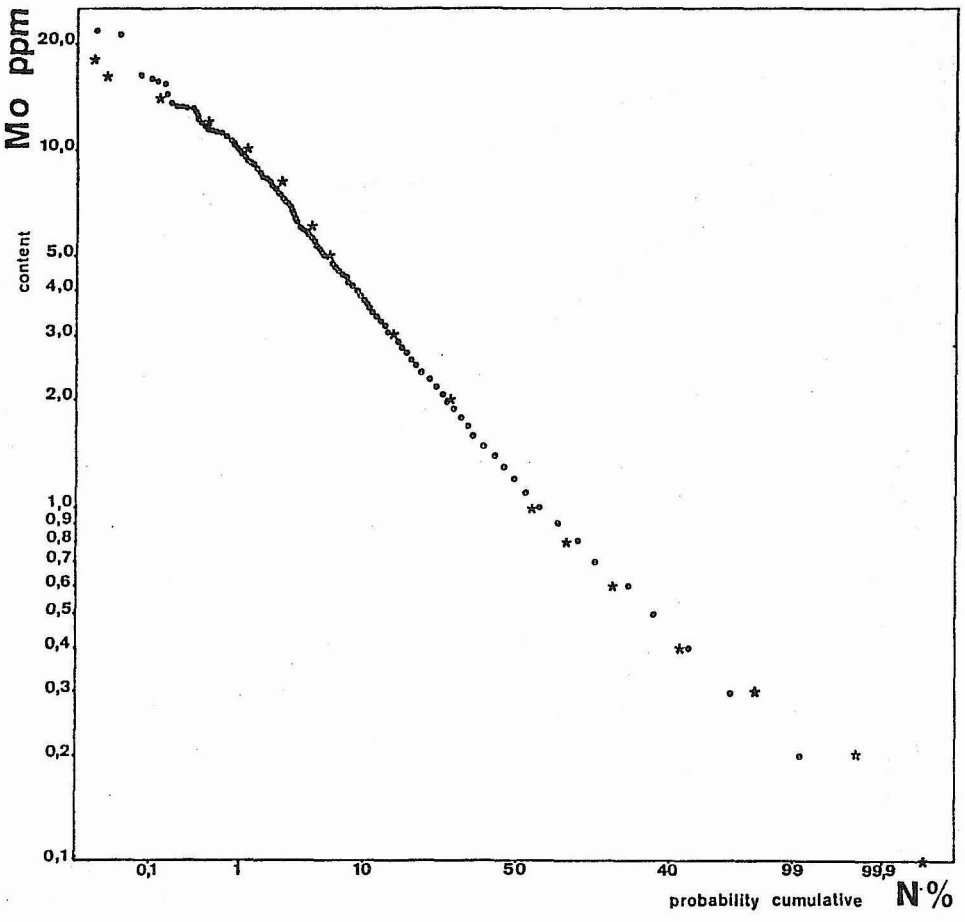


Fig. 1. Cumulative distribution function of molybdenum content in stream sediment of the area of the Dukla Folds and their margin

Points — empirical distribution delimited on a base of analytical data; stars — check points on a base of the probability graphs presented at the Fig. 2

Dystrybuanta rozkładu statystycznego zawartości molibdenu w osadach aluwialnych obszaru występowania fałdów dukielskich i ich obrzeża

Punkty — dystrybuanta empirycznie wyznaczona bezpośrednio na podstawie danych analitycznych; gwiazdki — dystrybuanta rekonstruowana na podstawie prostych Henry'ego z fig. 2

Statistical distribution of the molybdenum content in active stream sediment of the Beskid Niski Mts., Bieszczady Mts. and Doły Jasielsko-Sanockie has been presented at the Fig. 1. The diagram points represent an empirical Mo distribution. Statistical distribution of the molybdenum content in the analysed samples shows the three-modal distribution. Two characteristic points indicate: a distinct inflection at about 6.5 ppm Mo and a slight deflection at about 1.0 ppm. Presence of the inflection point mean that there are two populations combined in a limited part one to another. Presence of the deflection point

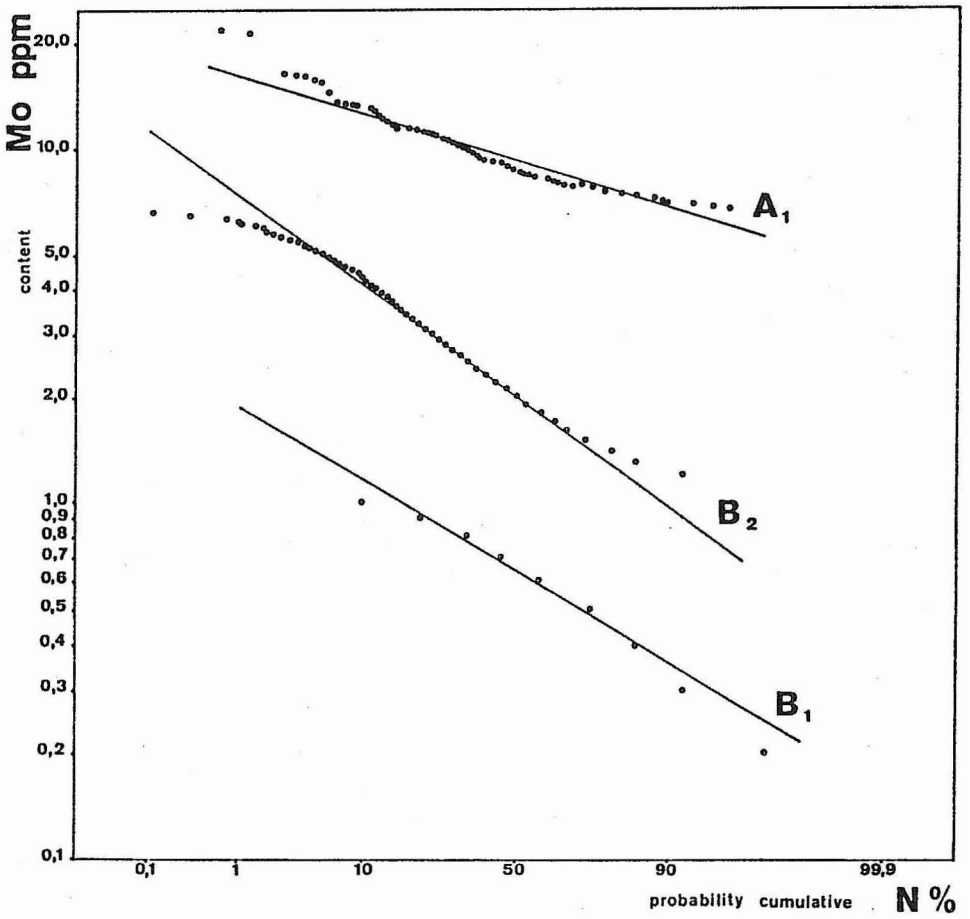


Fig. 2. Graphic interpretation of statistical distribution of molybdenum content in alluvial sediments of the area of occurrence of the Dukla Folds and their margins

A_1 — distribution curve for the anomalous population; B_1, B_2 — distribution curves for the populations of geochemical background; partition points: 1.0 and 6.5 ppm Mo; the probability graphs show the theoretical distribution curves for the populations A_1, B_1 and B_2

Interpretacja graficzna rozkładu statystycznego zawartości molibdenu w osadach aluwialnych obszaru występowania fałdów dukielskich i ich obrzeża

A_1 — dystrybuanta podzbioru anomalnego; B_1, B_2 — dystrybuanty podzbiorów tła geochemicznego; punkty podziału: 1,0 i 6,5 ppm Mo; proste Henre'ego wyznaczają przebieg dystrybuanty teoretycznej podzbiorów A_1, B_1 i B_2

would mean there are a three populations interferring in a widespread part one to another. The hypothetic populations have been separated with the partition points 1.0 and 6.5 ppm Mo. Probability graphs delimited on this basis and results of this partition has been presented at the Fig. 2. Reconstruction of the partition lines and the corresponding points has been marked at the Fig. 1. Good coincidence of distribution of the points at the

Table 1

Statistical characteristics of the subpopulations

Subpopulation	Number of samples	Proportion (%) of subpopulation	Geometric mean [Mo ppm]	Cumulative percentils [Mo ppm]	
				16%	84%
A_1	157	3.0	9.0	10.8	7.3
B_1	2633	50.1	2.0	3.5	1.1
B_2	2462	46.9	0.7	1.0	0.4

theoretical and reconstructed distributary curves between 0.1 and 95% of cumulative probability is visible. Marginal parts of the distributions are more divergent for the reason of low frequency of marginal statistical classes.

The general population of all measurements of molybdenum content in stream sediment of Beskid Niski Mts. and Bieszczady Mts. consists probably of three subpopulations with statistical characteristics presented in the Table 1.

The subpopulation A_1 may be accomplished with a good probability as a groupe of anomalous Mo content on a base of high values of the Mo content and low contribution of it in the general population. The subclasses B_1 and B_2 can be accomplished as two different subclasses of a geochemical background on a base on their great frequency and relative low values of the Mo content.

AREAL DISTRIBUTION OF MOLYBDENUM

Two geochemical maps: the contours map one (Fig. 3) and the point-symbol one (Fig. 4) present spatial distribution of molybdenum in stream sediment of the studied part of the Carpathian Mts. Computer program MAPART–2, worked out in the Polish Geological Institute (J. Owczarczyk et al., 1980), has been used during preparation of the contours map. More than ten of areas with increasing molybdenum content in stream sediment have been fixed there. These areas are mostly elongated according to the NW–SE direction. Some areas may be conspicuous after their size and amplitude of the Mo content. There are as follows:

1. Zubracze — Wola Michowa area. Area about 10 km long elongated according to the NW–SE direction along the Osława river, from Wola Michowa village to Zubracze village on the Solinka river. This area belongs to the Komańcza — Wisłok Wielki Fold. Extremal molybdenum content amounts 22.1 ppm.

2. Deszno — Rudawka Rymanowska area. Increasing molybdenum concentrations have been observed in tributaries of Pielnica, Wisłok, Tabor and Iwonka rivers. The area of its occurrence is a narrow belt about 20 km long. The highest molybdenum content has been notified to the SW of Głębokie village and it amounts 13.2 ppm. This area belongs to the Iwonicz — Rymanów — Baligród Anticline.

3. Kalnica area. Increasing molybdenum concentrations have been observed in stream sediment of the Kalniczka river and its tributaries and of the tributaries of the Hoczewka

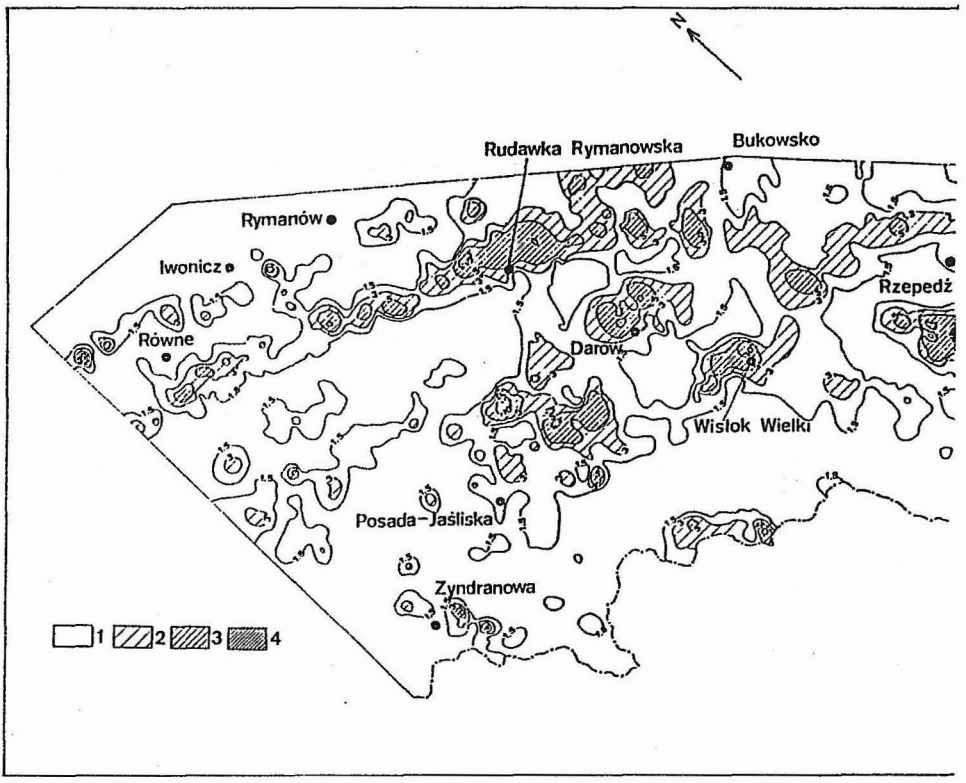
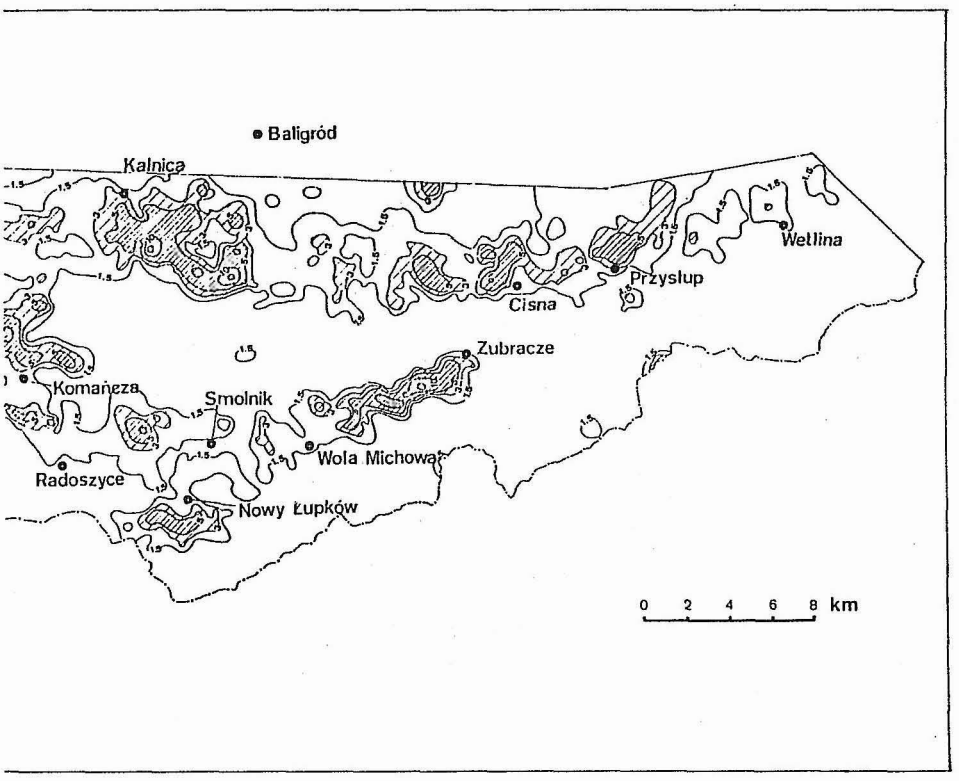


Fig. 3. Geochemical molybdenum contours map of the area of occurrence of the Dukla Folds and their frames
Molybdenum content (in ppm): 1 — 1.5–3, 2 — 3–5, 3 — 5–10, 4 — >10

river. This anomaly is placed at the Iwonicz — Rymanów — Baligród Anticline area. Extremal molybdenum contents have been observed in stream sediment of one of the tributaries of the Tarnawka river (16.4 ppm) and of the Rabiański Potok creek (15.6 ppm).

4. Posada-Jaśliska area. Increasing molybdenum concentrations have been observed in stream sediment of tributaries of the Wisłok and Jasiołka rivers to the NE of Posada-Jaśliska village. This area belongs to the Marginal Fold. Extremal molybdenum concentration amounts 21.5 ppm.

5. Jabłonki — Cisna — Przysłup area. Increasing molybdenum concentrations in sediments of tributaries of the Wetlinka, Dołżyczka, Solinka and Jabłonka rivers have been marked an area 13 km long, elongated according to the NW–SE direction. This area belongs to the Iwonicz — Rymanów — Baligród Anticline. Extremal Mo-content has been notified to the north of Cisna village (10.6 ppm) and to the west of Przysłup village (10.8 ppm).



Izoliniowa mapa geochemiczna molibdenu obszaru występowania fałdów dukielskich i ich obrzeża
Zawartość molibdenu (ppm): 1 — 1,5–3, 2 — 3–5, 3 — 5–10, 4 — >10

6. Rzepedź — Komańcza area. Two neighbouring areas with increasing molybdenum concentration belong to this area. The bigger one covers stream sediment of tributaries of the Osława and Osławica rivers and it belongs to the Marginal Fold. Extremal molybdenum content (13.2 ppm) has been fixed in one of the tributaries of the Jawornik river to the east of Rzepedź village. The second, smaller area is located to the south of Komańcza village and it belongs to the Komańcza — Wisłok Wielki Slice. Extremal molybdenum content in stream sediment amounts 11.6 ppm there.

7. Bukowsko — Szczawne area. Increasing molybdenum concentrations in stream sediment of tributaries of the Goryłka, Silska and Graniczny Potok creeks have been marked at area about 12 km long. This area belongs to the Iwonicz — Rymanów — Baligród Anticline. Molybdenum content above 10 ppm has been fixed to the west of Szczawno and Bukowsko villages.

8. Wisłok Wielki area. Increasing molybdenum content has been notified in stream sediment in two small areas. The first one is placed between the Dział and Skibice hills

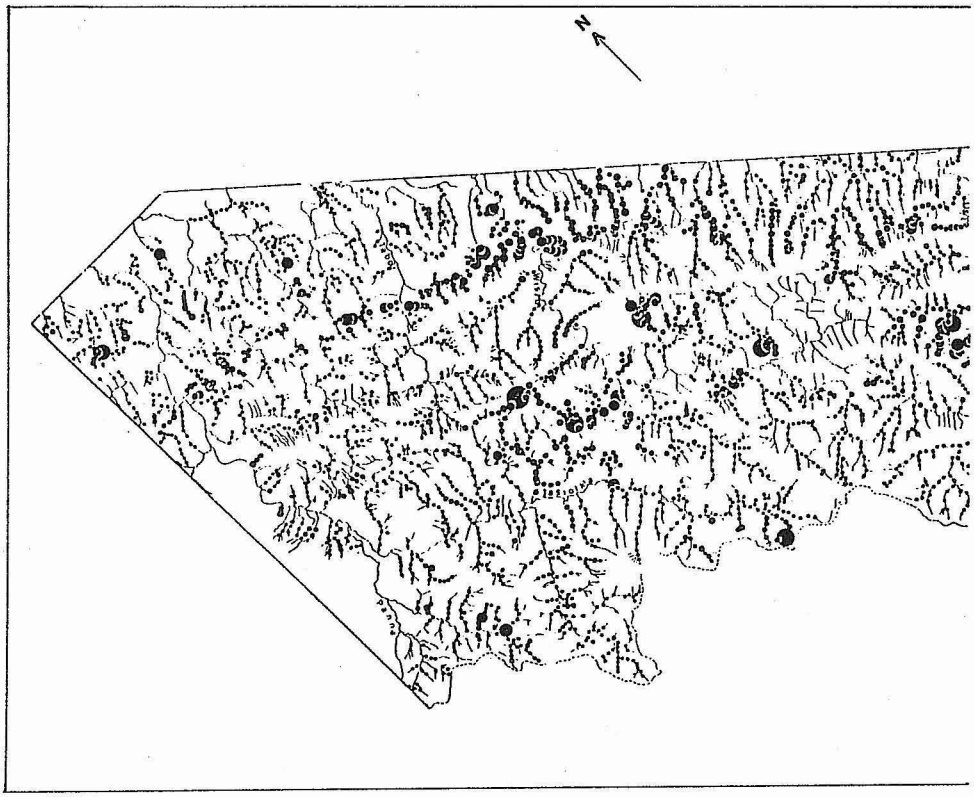
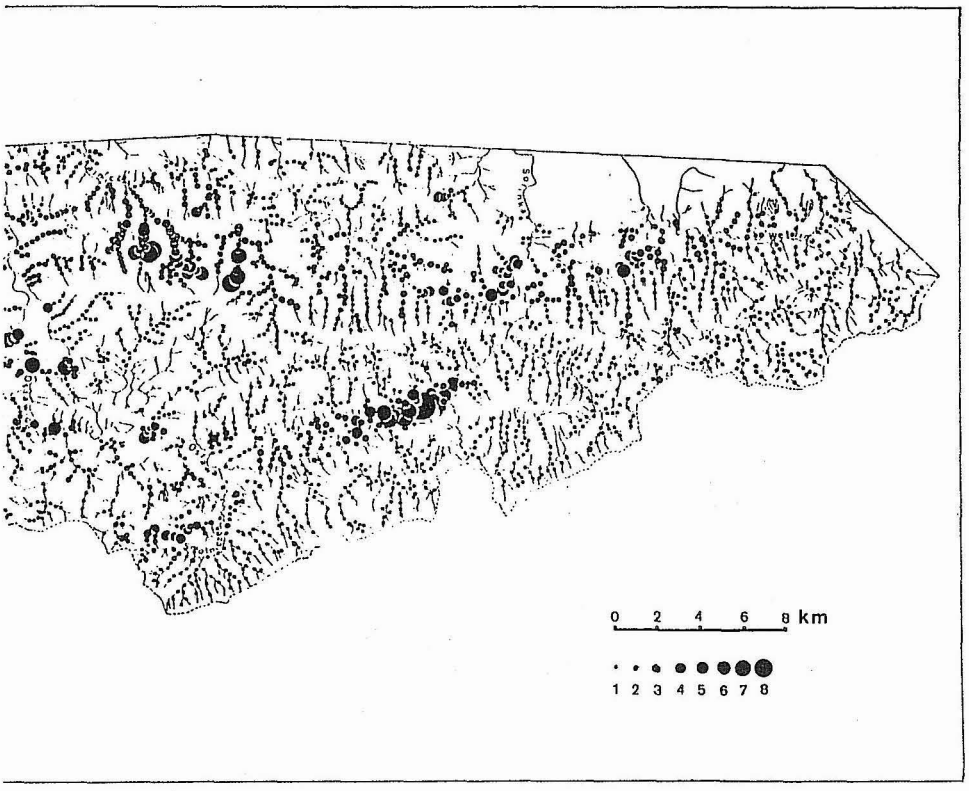


Fig. 4. Geochemical molybdenum point-symbol map of the area of occurrence of the Dukla Folds and their frames
Molybdenum content (in ppm): 1 — < 2, 2 — 2–4, 3 — 4–6, 4 — 6–8, 5 — 8–10, 6 — 10–12, 7 — 12–14, 8 — 14–16

and it belongs to the Marginal Fold. Molybdenum content amounts 16.8 ppm there. The second area is placed to the north of Wisłok Wielki village and extremal molybdenum concentration amounts 16.2 ppm there.

9. Nowy Łupków area. Increasing molybdenum content has been notified in stream sediment in two small areas. The first one covers river head tributaries of the Smolniczek creek to the SW of Nowy Łupków village and it belongs to the Pasieka Fold. Increasing molybdenum concentrations amounting 9.3 and 9.0 ppm have been notified there. The second area is placed in one of the Osława river tributaries to the east of Mików village. This area belongs to the Komańcza — Wisłok Wielki Slice. Molybdenum content amounts 11.1 ppm there.

10. Bóbrka — Równe — Lubiatowa area. Two neighbouring areas with increasing molybdenum concentration belong to this area. Both of them belong to the Bóbrka — Rogi — Klimówka Fold. The first one is placed to the south of Bóbrka village and extremal increasing molybdenum content in stream sediment amounts 13.2 ppm there.



Punktowa mapa geochemiczna molibdenu w obszarze występowania fałdów dukielskich i ich obrzeża
Zawartość molibdenu (ppm): 1 — <2 , 2 — 2–4, 3 — 4–6, 4 — 6–8, 5 — 8–10, 6 — 10–12, 7 — 12–14, 8 — 14–16

The second one is placed to the south of Równe village and it is elongated according to the NW–SE direction. Molybdenum content in stream sediment exceeds 4 ppm there.

DISCUSSIONS OF RESULTS

Analysis of the molybdenum geochemical maps and the geological map of the studied area has shown the relation between geological setting of this area and molybdenum concentration in stream sediment. Areas of increasing molybdenum concentration assume belts on both the geochemical maps of the eastern part of the Bieszczady Mts., western part of the Beskid Niski Mts. and northern part of the Doły Jasielsko-Sanockie (Figs. 3 and 4). Orientation of the belts (NW–SE) is concordant to strike of anticlines and slices

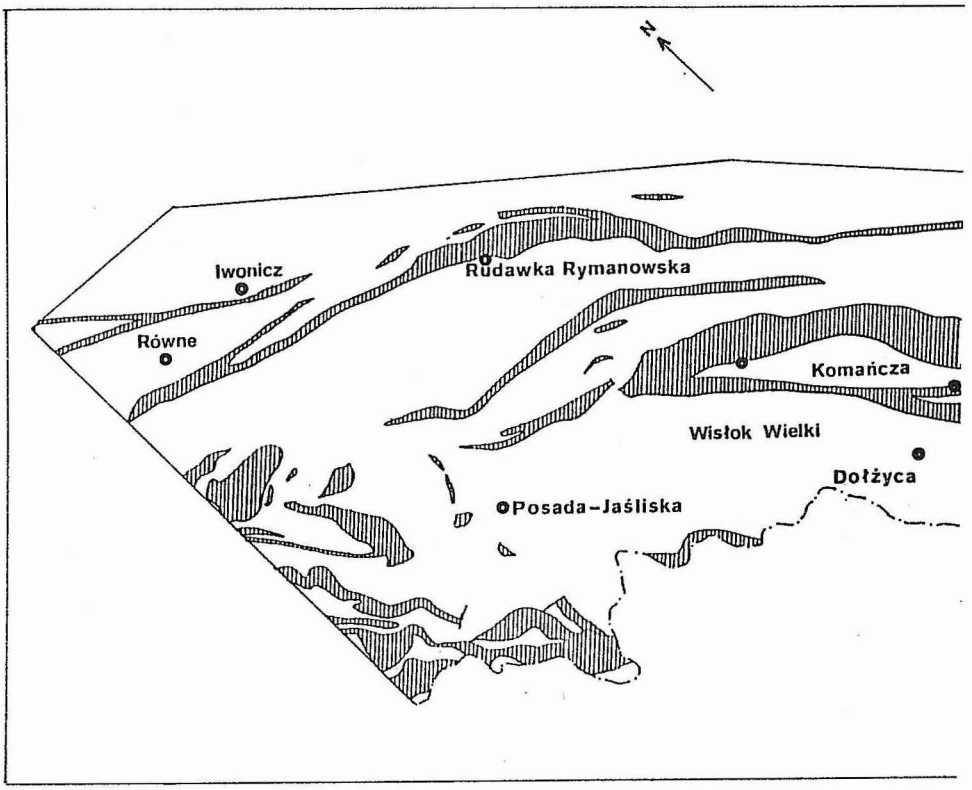
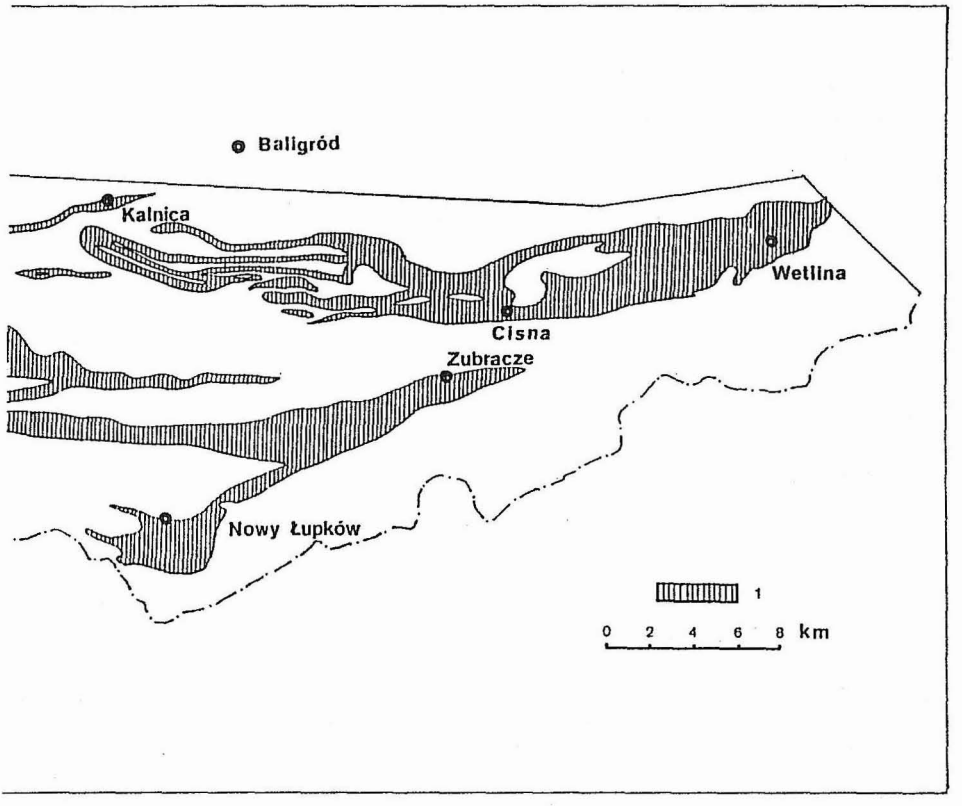


Fig. 5. Occurrence of the Menilite Beds on the area of the Dukla Folds and their frames (H. Świedziński, 1958)
1 — Menilite Beds

of the Dukla Folds and Silesian Nappe. Areas of increasing Mo-content (Fig. 5) are agree with the places of occurrence of Menilite Beds (H. Świdziński, 1958).

Geochemical analysis of the Carpathian Flysch sedimentary rocks made by I. Gucwa and T. Wieser (1980) comprised fixing of content of some trace elements: vanadium, molybdenum, nickel, cobalt, copper, chrome, manganese and zinc. These examination showed increasing molybdenum content in the Menilite Beds (35 ppm in average) and in the Hieroglyphic Beds (18 ppm in average). In the other rock series of the Cieszyn, Wierzowa, Lgota, Istebna and Krosno Beds average molybdenum content amounted about 3 ppm. Positive correlation with organic carbon ($r = 0.59$) (I. Gucwa, T. Wieser, 1980) has explain higher molybdenum concentration in the Menilite Beds as an effect of its biogenic accumulation.

From among of statistically distinguished two subclasses of molybdenum geochemical background in studied stream sediment, the B_2 population is related to occurrence of the molybdenum-scanty rocks (beds: Cieszyn, Wierzowa, Lgota, Istebna, Krosno). The



Występowanie warstw menilitowych na obszarze fałdów dukielskich i ich obrzeża (H. Świedziński, 1958)
1 — warstwy menilitowe

B_1 population is related to the more molybdenum-rich rocks of the Menilite Beds. Contour line 1.5 ppm limits these areas on the geochemical contour map and points with molybdenum content above 2 ppm mark these areas on the geochemical point map. In the areas of the increased molybdenum background distinguished in subpopulation A_1 there have been observed samples of stream sediment with high Mo-content. That high molybdenum content is probably related to the occurrence of extremely molybdenum-rich parts ot the Menilite Beds, because molybdenum contents in some samples of the rocks of this formation reaches even to 155 ppm (I. Gucwa, T. Wieser, 1980).

CONCLUSIONS

1. Some areas with increased molybdenum content, elongated according to the NW–SE direction, have been fixed in recent stream sediment in the western part of the Bieszczady Mts., eastern part of the Beskid Niski Mts. and southern margin of the Doły Jasielsko-Sanockie.

2. Comparison of the geological map of the studied area with the geochemical molybdenum maps shows the relation between location of the areas with increasing molybdenum content in stream sediment and occurrence of the Menilite Beds.

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Izabela BOJAKOWSKA, Jerzy BORUCKI

MOLIBDEN W OSADACH ALUWIALNYCH NA OBSZARZE WYSTĘPOWANIA FAŁDÓW DUKIELSKICH I ICH OBRZEŻA

Streszczenie

Na obszarze o powierzchni około 1700 km^2, obejmującym zachodnią część Bieszczadów, wschodnią część Beskidu Niskiego i południowy skraj Dołów Jasielsko-Sanockich, wykonano badania geochemiczne osadów aluwialnych. Do badań pobrano 5252 próbki przy gęstości opróbowania 4 punkty na 1 km^2. W próbkach tych oznaczono m.in. zawartość molibdenu metodą ASA z zastosowaniem atomizacji elektrotermicznej.

Zawartość molibdenu w osadach aluwialnych mieści się w przedziale od 0,1 (granica czułości metody) do 22,1 ppm (średnia 1,25 ppm). Na podstawie danych analitycznych wykreślono izoliniową i punktową mapę geochemiczną molibdenu. Na mapach geochemicznych stwierdzono obecność szeregu stref o przebiegu NW–SE, charakteryzujących się podwyższonymi zawartościami molibdenu w osadach aluwialnych. Porównanie mapy geologicznej badanego rejonu z mapami geochemicznymi molibdenu wskazuje na związek między występowaniem obszarów o podwyższonej zawartości tego pierwiastka we współczesnych aluwiach badanej części Karpat a występowaniem warstw menilitowych.