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VANADIUM IN THE COPPER ORE DEPOSIT ON THE FORE-SUDETIC MONOCLINE (POLAND)

UKD 550.422/.423:546.881:553.43:551.736.3:549.623:552.52+552.543(438—14 monoklina przedsudecka)

Abstract. Vanadium occurs in the Lower Zechstein shale and clay dolomite mainly in the form of organic compounds — vanadyl ethioporphyrins. Electron microprobe studies have shown that it concentrates in organic matter located between the flakes of clay minerals. Maximum vanadium content in microareas may run up to 5 wt.%, averaging 0.11 wt.% in shale. The vertical distribution of this metal in the ore-bearing sequence is independent of the intensity or type of mineralization.

INTRODUCTION

Vanadium content in the copper ore deposit of the Fore-Sudetic monocline is correlated with the lithologic types (sandstone, shaly, dolomitic) of ore. The highest V content has been noted in shale (Table 1), and has been reported as typical of rocks of this type from different parts of the world (Vine, Tourtelot 1970). About 39 tons of V per year is recovered from a similar "Kupferschiefer" deposit in Mansfeld, Germany (Schüller 1959). Microscopic and electron microprobe studies failed to confirm the earlier assumptions of Wojciechowska and Serkies (1969) that vanadium forms its own mineral phases: patronite (VS_2) or quisquite (vanadium-bearing variety of brown coal). Neither does it form any substantial admixtures in sulphide minerals. Studies of clay-organic shales made by Tokarska (1971) on chloroform extracts point to the presence of trace amounts of vanadyl porphyrin complexes. It has been assumed, therefore, that the principal carriers of vanadium are organic compounds forming kerogen, and presumably also clay substance. It is generally known that vanadium shows a tendency to concentrate in bitumens and coals. It is also readily adsorbed by colloidal Fe and Al compounds and by clay minerals.

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Table 1

Basic statistical parameters calculated for vanadium contents at different mining fields

Mine fields	Ore lithology	Weighted average (wt. %) (\bar{x})	Standard deviation (s)	Variability coefficient (%) (V)	Number of samples (n)
Rudna (all fields)	dolomite	0.0151	0.0197	130.69	91
	shale	0.1262	0.062	49.15	80
	sandstone	0.0065	0.0065	101.06	80
Lubin-West	dolomite	0.0138	0.025	180.65	70
	and lime-stone				
	shale	0.0989	0.106	107.43	34
Lubin-East and Lubin-Main	sandstone	0.0062	0.005	83.25	30
	shale	0.0883	0.0555	62.61	64
Polkowice (all fields)	shale	0.1172	0.0739	63.14	153
All fields of Lubin Copper Distr.	shale	0.1106			297

Calculations based on archival data collected by Geological Survey of Lubin Copper District.

EXPERIMENTAL

Shale samples enriched in vanadium were subjected to investigation with the aim of identifying organic compounds. Porphyrins were extracted using the method of Blumer and Omen (vide Eglington, Murphy 1969, p. 163). Carbonate minerals were dissolved in 2 n HCl. The insoluble residue was extracted with 1:1 benzol-methanol mixture and evaporated. The extract was dissolved in a small amount of chloroform and asphaltenes were precipitated with hot isooctane. The precipitate was filtered and washed with a mixture of chloroform and isooctane. The filtrate was evaporated and dissolved in diethyl ether, whereupon it was extracted successively with HCl solutions of concentrations of 2.4, 4.9 and 6.1 n. The first extract was neutralized with sodium acetate and porphyrins were precipitated with ether.

Organic groups were identified by the method of infrared absorption on a Perkin-Elmer 580 spectrometer at the Institute of Petroleum Technology in Cracov. Spectra in visible range were recorded with a Perkin-Elmer 575 spectrometer.

Vanadium content was determined with a Puy-Unicam SP-90 B atomic absorption spectrometer. Samples were decomposed in three stages (boiling 4:1 HClO₄—HNO₃ mixture, HF and HNO₃), using air-acetylene flame for atomization. Standard solutions were prepared in anionic forms precisely corresponding to the samples studied. A blank determination was also made, taking into account the influence of matrix effects and the interaction of ions present in the solutions. Errors of determination did not exceed 0.0X wt. %. The determinations were made by J. Tarkowski and M. Sikora at the Department of Mineralogy and Geochemistry, Institute of Geology and Mineral Deposits.

Electron microprobe studies were carried out on an ARL-SEMQ X-ray micro-analyser, using standard instrument settings (accelerating voltage 20 kV, probe current 120—150 μ A). Elements were determined on the K α line, using the following standards: Si — KAlSi₃O₈, Mg—MgCO₃, Ca—CaCO₃, Cu — 100%, V — 100%, Fe and S — FeS₂, C — graphite, N — BN.

Moreover, archival materials ("complete" analyses) collected by the Geological Survey Unit of the Lubin Copper Mining District were included.

RESULTS

Correlation of vanadium with other metals and chemical compounds

Vanadium shows a distinct correlation with molybdenum in all lithologic types of ore and with C_{org} in shale. The latter relationship was established earlier by Harańczyk (1961). These positive correlations confirm the well known fact that vanadium tends to concentrate in organic compounds, and this seems to point to a reducing environment in which this element has precipitated. This statement is also borne out by studies of Kucha (1976). This author detected MoS₂ with X-ray methods in extracts of organic matter derived from shale. These are presumably very fine molybdenite grains (less than 2 μ m) isolated completely by organic particles. Organic matter indisputably played a significant part in the reduction of Mo. This may account for the existence of distinct V — Mo, V — C_{org} and Mo — C_{org} correlations (Table 2). Vanadium also shows a significant positive correlation with cobalt and nickel (Table 2) in carbonate rocks and shale.

Table 2

Pearson correlations coefficients of vanadium with other elements and compounds from the Lubin copper deposits Critical values "r" after Zieliński (1972) for $\alpha=0.05$ and $\gamma=n-2$

Compounds	Lubin-West*			Rudna			Lubin and Polkowice			
	Dl	Sh	Ss	Dl	Sh	Ss	Dl	Sh	Ss	Mz
SiO ₂	0.09	0.29	0.41	0.22	0.18	-0.48				
Al ₂ O ₃	0.18	-0.43	-0.04	0.21	0.14	0.51	0.16	0.88	0.12	0.41
C _{org}	0.37	0.47	-0.05	0.57	0.32	0.24	0.87	0.86	0.47	0.75
S _{sulf.}	0.45	0.27	-0.21	0.20	-0.05	0.19	0.13	-0.71	-0.17	
Fe	0.10	0.27	-0.24	0.12	-0.14	0.09				
Cu				0.29	0.03	0.34	-0.09	-0.34	-0.17	
Ag	0.55	0.21	-0.17	0.46	0.17	0.25	0.32	0.48	-0.09	
Co	0.87	0.55	0.55	0.38	-0.01	0.03	0.90	0.29	0.04	0.73
Ni	0.43	0.76	-0.04	0.56	0.01	0.32	0.83	0.73	-0.06	0.66
Zn	0.29	0.02	0.23	0.52	-0.03	0.08				
Pb	0.29	0.02	0.25	0.53	-0.02	0.14				
CaO	-0.16	-0.27	0.11	-0.26	-0.25	0.60				
MgO	-0.13	-0.33	0.14	-0.20	-0.17	0.30				
Mo	0.93	0.75	0.34	0.61	0.23	0.29	0.93	0.35	0.68	
Number of samples	70	34	30	81—96	70—84	78—80	85	84	84	84
Critical values	0.23	0.32	0.35	0.19	0.21	0.22	0.21	0.21	0.21	0.21

* — after Kucha and Sawłowicz (1980).

Dl — dolomite and/or limestone, Sh — shale, Ss — sandstone, Mz — whole mineralized zone.

The distribution of vanadium in the vertical column of the deposit is closely connected with the lithology of rocks. This is evidenced by weighted averages calculated for respective lithologic types of ore from various mine fields (Table 1). Average V content in sandstone is about 0.006 wt. %, being similar for all the mine fields (Table 1). The content of vanadium in the vertical profile of sandstone is essentially similar, commonly fluctuating about the above average and rarely exceeding 0.01 wt. % (Fig. 1). It is worth noting that the top part of sandstone cemented with carbonates is poorer in vanadium. This fact implies that vanadyl porphyrins did not take part in advanced diagenetic processes.

The highest vanadium concentrations have been found in shale (Fig. 1). The average content calculated for the whole deposit (297 samples) is 0.11 wt. % (Table 1). Shale also shows greatest variations in V content: from 0.003 to 0.4 wt. % according to the authors' data and up to 0.53 wt. % according to Serkies and Wojciechowska (1969).

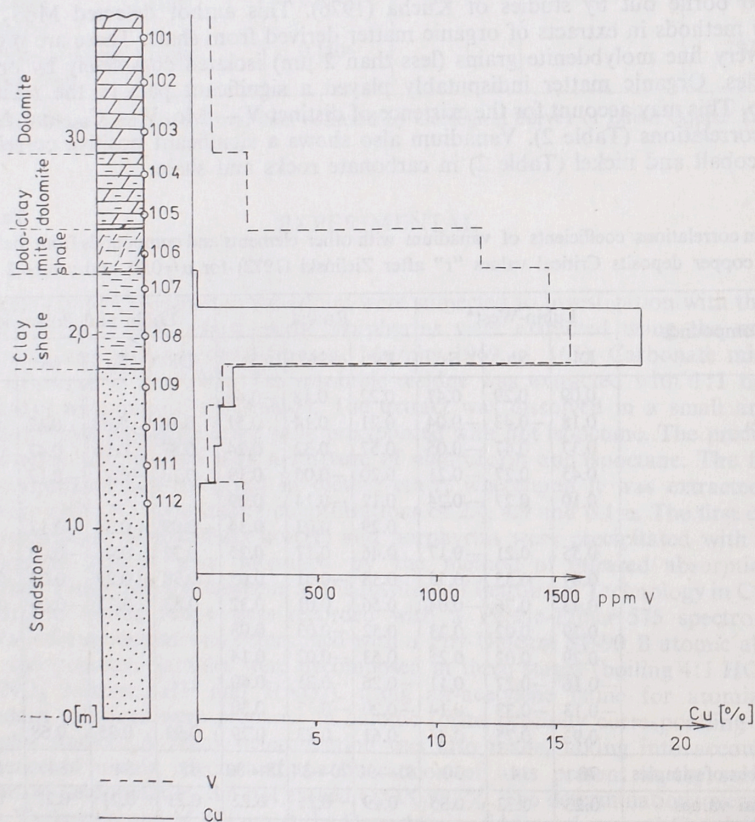


Fig. 1. Distribution of vanadium and copper in the vertical sequence of mineralized zone. Rudna mine

Worth noting is vanadium distribution in the transition zone between dolomitic shale and clay dolomite and within clay dolomite. The thickness of this zone, including clay dolomite, is usually twice to three times greater than the thickness of the underlying shale, while average V contents are generally similar to those in shale. However, the zone in question shows considerable vertical variation in V content. The zone adjacent to shale is enriched in vanadium, whereas the overlying carbonate rocks are considerably poorer in this element. In general, its content decreases towards the top of the mineralized zone (Fig. 1). On the average, carbonates contain twice as much vanadium as sandstone ore, and its concentrations bear no relation to the type of mineralization (Fig. 1). Sulphides of the Zn—Pb and Fe type occur immediately above copper mineralization, whereas the decrease in V content has been noted only at the dolomitic shale — clay dolomite lithologic boundary (Fig. 1).

The horizontal distribution of vanadium is controlled by the occurrence of shale. Areas in which shale does not occur are poor in this metal. The following regularity has emerged: the Rudna mine shows the highest average V content and the lowest variability coefficient (Table 1). The average V content decreases in a SE direction while the variability coefficient increases respectively; thus, vanadium content increases along the strike with a deviation to NNW.

ORGANOMETALLIC VANADIUM COMPOUNDS

Because of the lack of V ore minerals or vanadium-bearing minerals, the present investigations were mainly focussed on organic matter. Electron microprobe studies of the clay-organic matrix have revealed that vanadium forms concentrations distinctly located between the flakes of clay material (Fig. 2). The concentrations are up to 5—10 μm in size and V content may run up to 5 wt. %, averaging 1—2 wt. %. In secretional kerogen, displaced diagenetically beyond the shale, vanadium is present in trace amounts. This suggests a low mobility of this element during diagenesis.

To define accurately the relation between V and organic matter, an extract of benzol-methanol mixture enriched in vanadyl porphyrins (sample Sz4 — 293) was subjected to investigations. The untreated sample contained 0.3 wt. % V. Absorption spectra in the visible range disclosed strong absorption bands at 570 and 531 nm, typical of vanadyl ethioporphyrins (Eglinton, Murphy 1969), thus providing direct evidence of the existence of vanadyl porphyrins. The quantitative relations of absorption peaks suggest that all vanadium is combined in porphyrins. At the same time, weak absorption bands have been recorded at 550 and 590 nm, testifying to the presence of a small amount of simple alkyloporphyrins (ethio-types) of bivalent cations (Mg, Fe) (Eglinton, Murphy 1969).

INFRARED ABSORPTION SPECTROSCOPY

Organic extract enriched in vanadyl porphyrins was subjected to infrared absorption studies (Fig. 3). Intense absorption from alkane CH_3 , CH_2 and CH groups appears in the region of CH stretching vibrations, confirmed in the range of CH bending vibrations by absorptions arising from C—CH_3 and $\text{—CH}_2\text{—}$ groups, with $\text{—C—(CH}_3)_2$ group present in a subordinate amount. The absence of the 720 cm^{-1} band indicates that the length of unbranched alkane chain is less than 4 methylene groups.

Two distinct bands centered at 3040 and 3070 cm^{-1} appear in the range of aromatic CH stretching absorption (Fig. 3). They have been attributed to =C—H

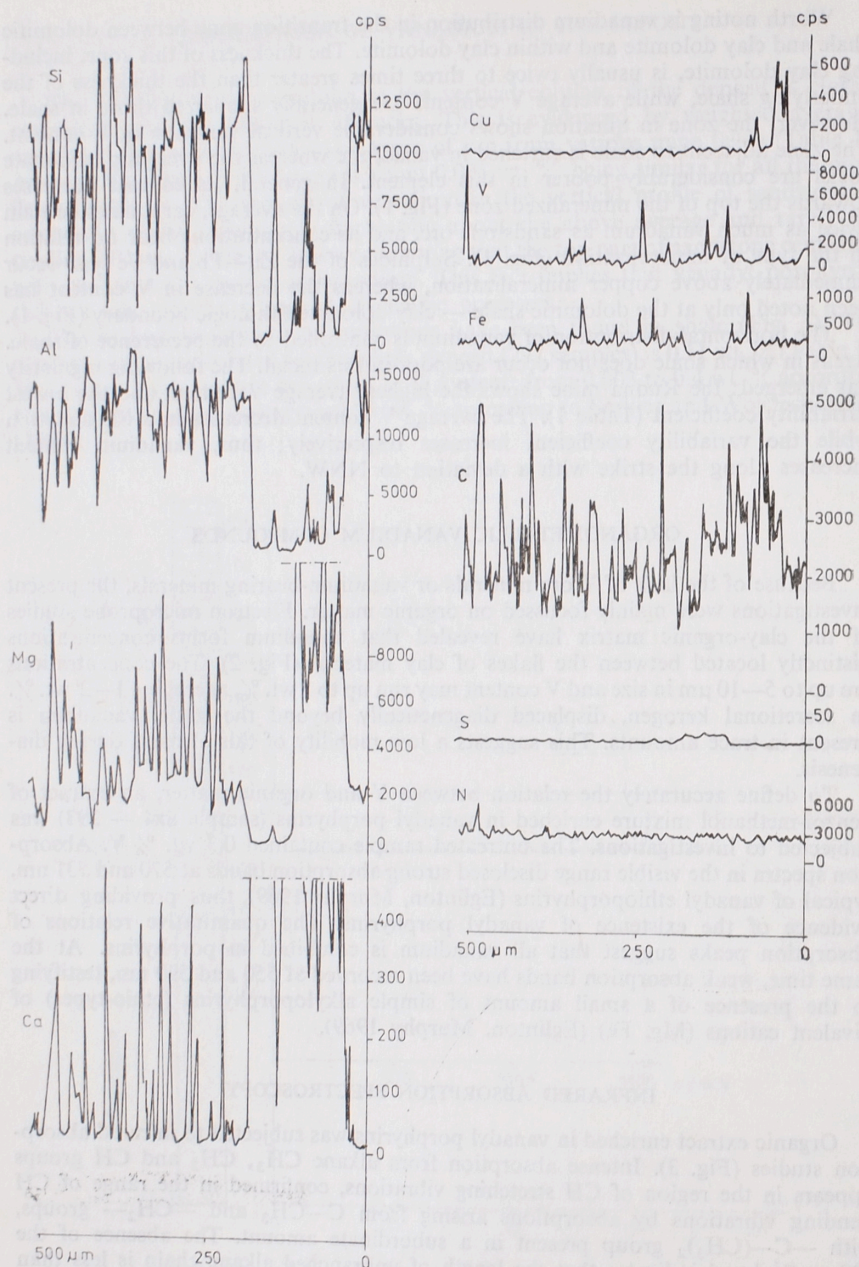


Fig. 2. Concentrations of Si, Mg, Al, Ca, Cu, V, Fe, C, S, N in the microarea of the shale. Section vertical to the microlamination of the rock. Rudna mine, sample 102/3, ARL-SEM microprobe analyser

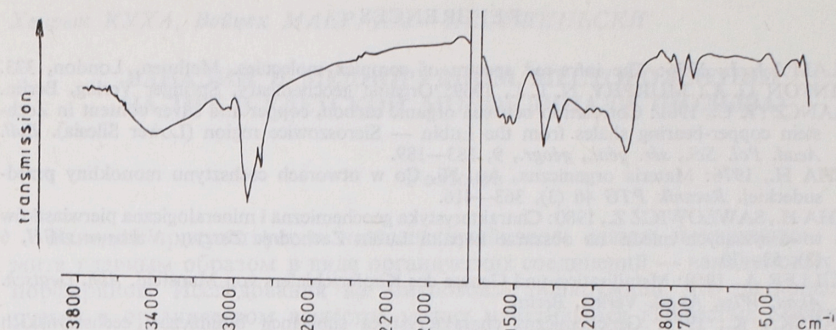


Fig. 3. IR-absorption spectrum of benzol-metanol extract from the copper-bearing shale. Polkowice mine, sample Sz4-293

stretching vibrations associated with aromatic and heterocyclic compounds. The lack of differentiation in absorption in the region between $2000-1660\text{ cm}^{-1}$ testifies to the presence of different substituents, none of them being prevalent. The above interpretation is borne out by absorption in the range of $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibrations and by the 1580 cm^{-1} absorption band, characteristic of heterocyclic rings (Bellamy 1956). A strong absorption band at $1000-1130\text{ cm}^{-1}$ is presumably due to the coincidence of ring vibrations and CH bending vibrations of pyrrole ring, various types of substitution of aromatic ring, and OH bending vibrations associated with the presence of amino acids. The latter also seem to be responsible for absorption bands in the regions above 1700 cm^{-1} and between 3100 and 3600 cm^{-1} , where amino, amide and OH groups are present. The $1600-1700\text{ cm}^{-1}$ band can be presumably assigned to the carbonyl group.

The extract under study consists mainly of alkanes, aromatic and heterocyclic-aromatic compounds and the pyrrole group. The aromatic and heterocyclic-aromatic compounds have relatively short alkyl substituents, such as alkanes, amino acids, ketones and probably phenols. In all likelihood, the same groups are present as well in branched alkanes not associated with aromatic ring.

CONCLUSIONS

1. Vanadium concentrations in the copper ore deposit on the Fore-Sudetic monocline are associated with the Lower Zechstein copper-bearing shale (Kupferschiefer) and in a less degree, with the lowermost part of the Zechstein limestone (Zechsteinkalk) profile.
2. Practically all vanadium present in the deposit is closely connected with organic matter. Compounds of the type of vanadyl ethioporphyrins are the principal carriers of this metal.
3. Vanadium concentrations show no relationship with the intensity or the mineralogical types of sulphide mineralization.

Translated by Hanna Kisielewska

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Henryk KUCHA, Wojciech MAYER, Adam PIETRZYŃSKI

WANAD W ZŁOŻU RUD MIEDZI NA MONOKLINIE PRZEDSUDECKIEJ (POLSKA)

Streszczenie

Wanad występuje w dolnocechsztyńskim łupku i dolomicie ilastym głównie w postaci związków organicznych — etioporfiryn wanadylowych. Badania chemiczne w mikroobszarze wykazały, że koncentruje się on w substancji organicznej, umiejscowionej pomiędzy blaszkami minerałów ilastych. Maksymalna zawartość wanadu w substancji organicznej może sięgać 5% wag., przy średniej zawartości dla łupka równej 0.11% wag. Rozmieszczenie metalu w profilu pionowym złoża jest niezależne od intensywności i typu okruszczowania.

OBJAŚNIENIA FIGUR

- Fig. 1. Rozmieszczenie wanadu i miedzi w profilu pionowym złoża Rudna.
- Fig. 2. Wykresy koncentracji Si, Mg, Al, Ca, Cu, V, Fe, C, S i N w mikroobszarze łupka. Analizę przeprowadzono prostopadłe do mikrolaminacji skały. Preparat 102/3, mikroskopia ARL-SEMQ.
- Fig. 3. Widmo absorpcyjne ekstraktu benzol-metanol z łupka miedzionośnego. Kopalnia Polkowice, próbka Sz4-293.

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ВАНАДИЙ В МЕДНОРУДНОМ МЕСТОРОЖДЕНИИ НА ПРЕДСУДЕТСКОЙ МОНОКЛИНАЛИ (ПОЛЬША)

Резюме

Ванадий присутствует в нижнецешихштейновом сланце и глинистом доломите главным образом в виде органических соединений — ванадиловых этиопорфиринов. Исследования на микрозонде обнаружили, что он концентрируется в органическом веществе между пластинками глинистых минералов. Максимальное содержание ванадия в органическом веществе может достигать 5 вес. %, при среднем содержании для сланца равным 0,11 вес. %. Размещение металла в вертикальном разрезе независимо от интенсивности и типа оруденения.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Размещение ванадия и меди в вертикальном разрезе месторождения Рудна.
- Фиг. 2. Концентрационные кривые Si, Mg, Al, Ca, Cu, V, Fe, C, S и N в микроучастке сланца. Анализ проведен вкост микрослойчатости породы. Препарат 102/3, микрозонд ARL-SEMQ.
- Фиг. 3. Абсорбционный спектр экстракта бензол-метанол из меденосного сланца. Рудник Польковице, образец Sz4-293.