MINERALOGIA POLONICA
Vol. 9, No 1 — 1978

*Marek MUSZYŃSKI *, Jacek RAJCHEL *, Witold SALAMON **

CONCRETIONARY IRON AND MANGANESE CARBONATES IN EOCENE SHALES OF THE ENVIRONS OF DYNÓW NEAR PRZEMYŚL (FLYSCH CARPATHIANS)

UKD 549.742.11.08:552.124.4'523:551.781.4(438-12 Dynów)

Abstract. Carbonate concretions occurring in Eocene shaly deposits of the Skole unit (Flysch Carpathians) have been examined using microscope, X-ray, infrared spectroscopic and chemical methods. The obtained results indicate that the concretions in Variegated shales and in Hieroglyphic Beds show different mineral composition. The former are represented by calcareous rhodochrosite or ponite. In the latter deposits the concretions consist of Ca-pistomesite and Ca-Mg-rhodochrosite, being sometimes accompanied by Mg-Fe-calcite. All the carbonates in question form disordered intergrowths within the concretions studied. Electron microprobe analysis has shown that even individual crystals and their aggregates display different proportions of Fe, Mg and Mn, whilst Ca distribution is rather constant. Iron and magnesium are usually concentrated in central parts of aggregates, whilst manganese — in their outer parts.

INTRODUCTION

Iron-manganese concretions were found in Eocene deposits of the Skole unit in the environs of Dynów—Dubiecko near Przemyśl (Rajchel 1976). They occur in Lower Eocene Variegated Shales and in overlying Middle, and partly Upper, Eocene Hieroglyphic Beds (Fig. 1). Similar concretions in other regions of occurrence of the Skole unit in the Flysch Carpathians have been studied by Narębski (1958) and described by Tokarski *et al.* (1961) and Kotlarczyk (1966), and in the Ukrainian Carpathians by Gabinet (1964, 1970, 1974).

Carbonate concretions in Lower Eocene Variegated Shales occur in green interlayers of these deposits, in upper part of the cross-section examined. They are irregular, cylindrical or discoidal in shape, being up to a dozen cm in diameter. Irregularly shaped concretions are usually smaller, showing uniform black or dark brown colouration. Their surfaces

* Academy of Mining and Metallurgy, Institute of Geology and Mineral Deposits, Cracow (30-059 Kraków, al. Mickiewicza 30).

are rough or smooth, brillant. Other concretions are pinkish-brown, being covered by brown-black weathering rim, several mm thick.

Within Hieroglyphic Beds, Fe-Mn concretions occur in the middle part of the cross-section (Pawłokoma) and in its upper one (Kosztowa). They are lenticular in shape and up to 15 cm thick, being gray-bluish in colour and covered with brown-ginger weathering crust.

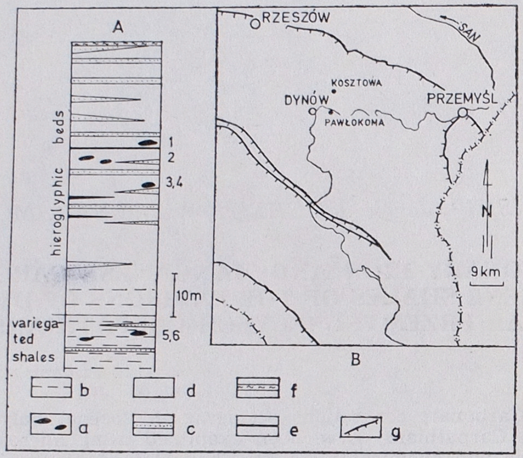


Fig. 1. Localization of sampling sites

A — synthetic lithological profil of the upper part of the Variegated Shales and Heroglyphic Beds in Dynów vicinity, B — schematic map,
1—6 — sample numbers, *a* — carbonate concretions, *b* — variegated shales, *c* — sandstones, *d* — green shales, *e* — green lydite, *f* — globigerine marls, *g* — main overthrust

The present authors have examined the mineral composition of several concretions collected from both the mentioned deposits. Identification of individual phases has been carried out using microscope observations, X-ray analysis, infrared absorption spectroscopy and chemical investigations.

EXPERIMENTAL PROCEDURE

Microscope observations have been carried out in transparent light using Polmi A. (Zeiss) microscope. X-ray study has been performed by means of powder method using Soviet DRON-1 diffractometer by applying monochromatic filtered CuK_α radiation. Infrared absorption spectra have been obtained by means of UR-10 spectrophotometer by applying KBr disk technique. Quantitative chemical analysis consisted in determination of Fe^{2+}, Mn^{2+}, Ca^{2+} and Mg^{2+}. The samples were dissolved in hot diluted (1 : 1) HCl. Manganese content has been estimated using AAS technicque by means of Pye Unicam SP-90B spectroscope and iron — by manganometric titration. The contents of calcium and magnesium have been determined using complexometric titration with Eriochrome Black and Kalces as indicators.

Chemical microanalysis of carbonate concretions has been carried out

by means of electron microprobe ARL SEMQ instrument, applying accelerating voltage 20 kV, current 120—150 μA and counting time 100 s. Spectrally pure Fe, Mg and Mn and CaF_2 of the same purity have been used as standards. Quantitaive point analysis and linear registration method have been used. In computing chemical composition of samples, corrections for difference in atomic number, fluorescence and absorption of radiation have been taken into account.

MICROSCOPIC EXAMINATIONS

In thin sections the samples in question represent evenly grained, fine-crystalline aggregates of carbonate minerals (Phot. 1, 2). The average grain-size varies from 0.002 to 0.01 mm and only locally ranges up to 0.06 mm. They are rather irregular in shape — euhedral grains are scarce. The carbonate matrix is locally, or sometimes totally, brownish coloured by iron and manganese oxides. In the latter case the thin section, when observed in transparent light, is nearly opaque.

Among secondary admixtures, there occur quartz grains, 0.015—0.07 mm in size, carbonized vegetal remains, hydromuscovite flakes, spherical glauconite and pyrite aggregates, as well as agglomerates of illitic clayey substance. In some samples there occurs agglutinated microfauna. Besides, the concretions from Hieroglyphic Beds contain microcrystalline silica, the amount of which may reach 40 vol. per cent. X-ray analysis has shown that it is low-temperature crystoballite (reflections: 4.10 (10), 2.98 (2), 2.497 Å (3) — Jones, Sanders, Segnit 1964).

Carbonate concretions in question display disordered, sometimes porous, textures. Locally they are veined with manganese or iron oxides, carbonates and chalcedony.

X-RAY AND INFRARED SPECTROSCOPIC INVESTIGATIONS

Concretions from Eocene Variegated Shales

Reflections due to carbonate phases in X-ray diffractometer patterns are sharp — showing no diffusion or duplications (Fig. 2). As follows from these data, individual concretions consist of one carbonate phase characterized by one complex of d_{hkil} reflections (Table 1), close to that reported for rhodochrosite or ponite (Narębski 1958, Lippmann 1973).

The above conclusions have been confirmed by the results of infrared spectroscopic analysis. In the range of absorption band ν_4, which is diagnostic for trigonal carbonates, there occur single maxima at 727 cm^{-1} (Fig. 3), indicating the presence of single carbonate phases, corresponding to rhodochrosite or ponite (Moenke 1962).

Concretions from Hieroglyphic Beds

In X-ray diffractometer patterns of individual samples (Fig. 2, Table 1), there occur simultaneously reflection complexes of two phases, close to siderite and to rhodochrosite, respectively (Lippmann 1973). Reflections

Table 1

Interplanar spacing (d_{hkl}) of concretionary iron and manganese carbonates from Eocene shales in the environs of Dynów (samples *1—6*)

Hieroglyphic Beds								Variegated Shales				Siderite (Lippmann 1973)		Rhodochrosite (Lippmann 1973)	
Sample No															
1		2		3		4		5		6					
$d_Å$	*I*	$d_Å$	*I*	$d_Å$	*I*	$d_Å$	*I*	$d_Å$	*I*	$d_Å$	*I*	$d_Å$	*I*	$d_Å$	*I*
3.648		3.640	1	3.663	1	3.678	2	3.668	3	3.663	4	—	—	3.6581	35
3.619		.619	3	3.597	2	3.597	1	—	—	—	—	3.5903	25	—	—
2.840		2.849	4	2.853	4	2 853	10	2.862	10	2.840	10	—	—	2.8440	100
2.809		2.797	10	2.800	10	2.797	10	—	—	—	—	2.7912	100	—	—
		—	—	—	—	—	—	2.652	0,5	—	—	—	—	2.6107	—
2.592		2.571	1	2.564	1	—	—	—	—	—	—	2.5622	—	—	—
2.382	2	2.398	1	2.398	1	2.392	2	2.395	2	2.374	2	—	—	2.3886	20
2.356	2	2.352	2	2.350	2	2.352	1	—	—	—	—	2.3443	20	—	—
2.161	2	2.181	1	2.177	1	2.176	2	2.186	2	2.176	2	—	—	2.1721	27
2.143	2	2.137	2	2.138	3	2.134	2	—	—	—	—	2.1318	27	—	—
2.000	2	2.003	1	1.998	1	2.003	2	2.010	2	2.002	2	—	—	2.000	23
1.975	2	1.971	2	1.969	2	1.973	1	—	—	—	—	1.9629	30	—	—
1.824	1	—	—	—	—	1.836	2	1.836	1	1.838	1	—	—	1.8290	12
1.799	1	—	—	1.797	1	1.821	1	—	—	—	—	1.7952	15	—	—
1.765	3	1.774	2	1.771	2	1.771	3	1.779	4	1.771	4	—	—	1.7698 1.7693	30 33
1.743	3	1.738	3	1.738	3	1.737	3	—	—	—	—	1.7369 1.7296	35 44	—	—
—	—	—	—	—	—	—	—	—	—	1.566	1	—	—	1.5559	1
1.535	1	1.539	1	1.539	1	1.537	1	1.545	2	1.535	2	1.5271	—	1.5334	13
1.510	1	1.509	1	1.506	1	1.514	1	—	—	—	—	1.5050	19	—	—
—	—	1.457	1	1.462	1	1.453	1	1.459	1	1.457	1	—	—	1.4649 1.4522	— 1
—	—	1.431	1	1.427	1	—	—	1.424	1	1.415	1	1.4377 1.4253	— 16	— 1.4220 1.4066	— — —
—	—	1.383	1	—	—	1.382	1	1.385	1	1.386	1	1.3956	7	1.3790	10

* 1 Å = 0.1 nm (SI).

corresponding to $FeCO_3$ are usually stronger than those due to $MnCO_3$, indicating quantitative dominance of the former phase. Sharpness and separation of reflections connected with these both phases are variable, confirming large compositional variations of the concretions studied.

Infrared absorption spectra also confirmed the above conclusion. In the range of ν_4 band their occur two absorption maxima: one 727—729 cm^{-1} (Fig. 3), corresponding to rhodochrositic phase, and second — 735—739 cm^{-1} — sideritic (Moenke 1962). Usually the latter maximum is higher than the former one, indicating dominance of sideritic phases.

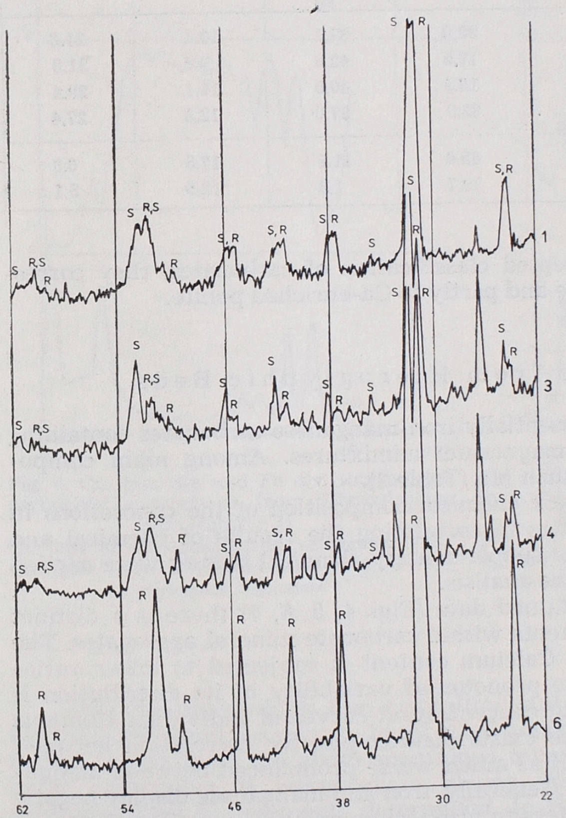


Fig. 2. X-ray diffractometer patterns of carbonate concretions from Hieroglyphic Beds (*1, 3, 4*) and Variegated Shales (*6*) of the environs of Dynów

R and *S* — reflexions of rhodochrositic and sideritic phases respectively

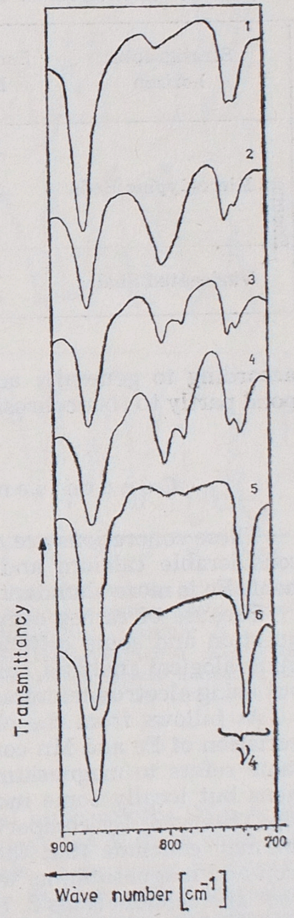


Fig. 3. Infrared absorption spectra of carbonate concretions from Hieroglyphic Beds (*1—4*) and Variegated Shales (*5, 6*) of the environs of Dynów

CHEMICAL ANALYSIS

Concretions from Variegated Shales

Chemical data indicate that these concretions consist predominantly of manganese carbonate containing iron, calcium and magnesium admixtures (Table 2). The proportions of the above cations are variable and thus,

Table 2

Chemical analyses of carbonate concretions from Variegated Shales and Hieroglyphic Beds in the environs of Dynów (Analysts: K. Dudek, M. Sikora, J. Tarkowski)

	Stratigraphic horizon	Sample No	Molecular content of individual carbonates			
			$MnCO_3$	$FeCO_3$	$CaCO_3$	$MgCO_3$
Eocene	Hieroglyphic Beds	*1*	30.9	37.1	10.4	21.6
		2	17.5	42.8	7.9	31.8
		3	16.5	40.0	14.1	29.4
		4	23.3	37.0	12.3	27.4
	Variegated Shales	*5*	65.0	11.2	17.5	6.3
		6	79.7	1.3	13.9	5.1

according to generally accepted classification of carbonates, they correspond partly to rhodochrosite and partly to Ca-enriched ponite.

Concretions from Hieroglyphic Beds

These concretions are essentially iron-manganese carbonates containing considerable calcium and magnesium admixtures. Among main components Fe is more abundant than Mn (Table 2).

Because of rather complex chemical composition of the concretions in question and some difficulties in correlating the results of chemical and mineralogical analyses, some supplementary chemical studies were carried out using electron microprobe analisis.

As follows from the obtained data (Figs 4, 5, 6, 7) there is a distinct variation of Fe and Mn contents within carbonate mineral aggregates. The same refers to magnesium. Calcium content is subjected to lower variations but locally some more pronounced variability of its distribution is also observed. By comparing concentration curves of individual elements we may conclude that there exists distinct positive correlation between iron and magnesium, as well as much worse pronounced between manganese and calcium (Figs 5, 7). Generally, iron and manganese display negative correlation. The same refers to magnesium and calcium (Figs 5, 6).

All the obtained data indicate that there are two essential components of the concretions studied:

— iron-magnesium carbonate
— Ca- and Mg-enriched manganese carbonate.

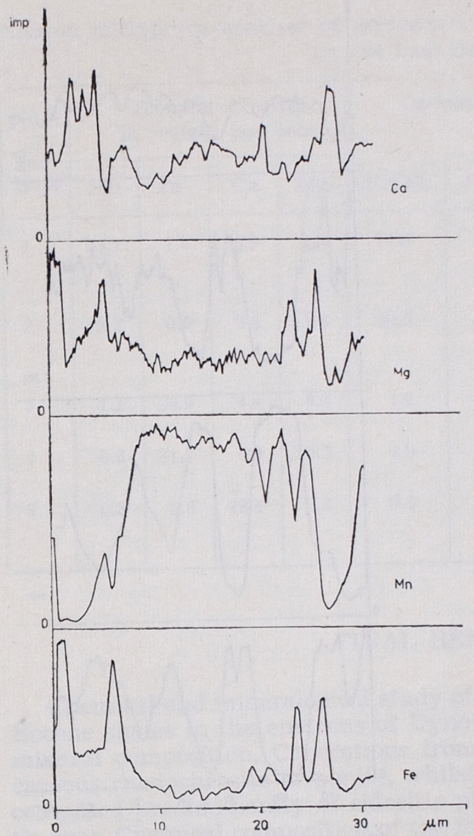


Fig. 4. Ca, Mn, Mg and Fe distributions in carbonate concretions from Hieroglyphic Beds (sample *3*)

The line of semi-quantitative microprobe analysis goes across a compact polycrystalline Mn-carbonate aggregate

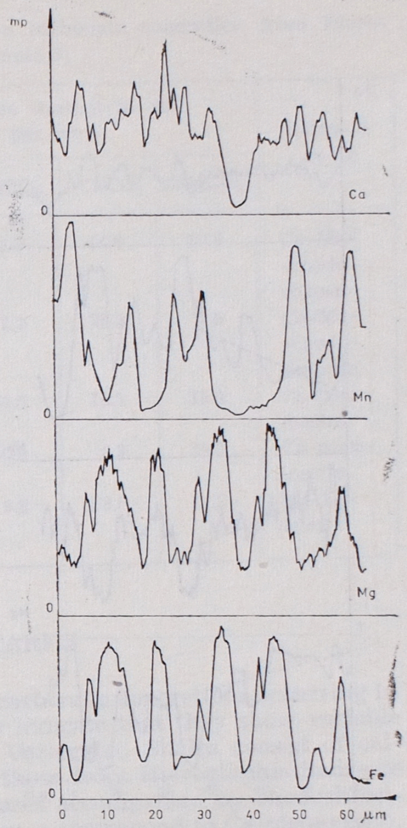


Fig. 5. Ca, Mn, Mg and Fe distributions in a carbonate concretion from Hieroglyphic Beds (sample *3*)

The line of semi-quantitative microprobe analysis goes across typical mutual intergrowths of Mn and Fe carbonates

These two phases form fine-crystalline mutual intergrowths (Figs 5, 7). On the other hand, no monomineral zonal concentrations of them were observed. Apart from the above mentioned minerals, there occur microgranular aggregates of intermediate phases (Fig. 6), containing variable amounts of all the elements determined. In these aggregates we observe the following regularity: the increase of Fe and Mg concentration in them is accompanied by increase or decrease of Mn, whilst the amount of Ca is fairly constant.

Quantitative point determination of elements have been carried out by means of electron microanalyser to find the chemical composition of

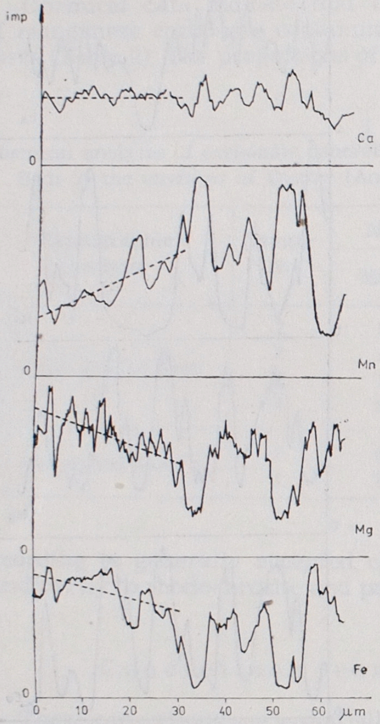


Fig. 6. Ca, Mn, Mg and Fe distributions in a carbonate concretion from Hieroglyphic Beds (sample *1*)
The left part of the line of semi-quantitative microprobe analysis goes across crystal aggregates showing gradular variations of contens of Fe, Mg and Mn. The decrease of Fe and Mg concretion is accompanied by increase of Mn, whereas Ca content remains fairly constant

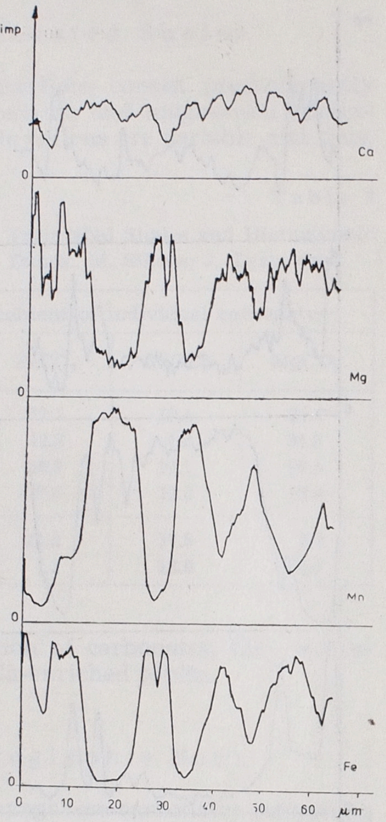


Fig. 7. Ca, Mn, Mg and Fe distributions in a carbonate concretion from Hieroglyphic Beds (sample *1*)
The line of semi-quantitative microprobe analysis goes across characteristic intergrowths of Mn and Fe carbonate phases

carbonate minerals studied (Table 3). The obtained results confirmed the presence of two main carbonate phases: ferrous (30—32 wt. % Fe) and manganous (33-37 wt. % Mn), containing other element admixtures. Calcium content is generally high, especially in manganese phases (Table 3, pos. *1*, *2*), whilst magnesium is related with $FeCO_3$ grains (Table 3, pos. *3*, *4*). Besides, there occur individual crystals consisting essentially of $CaCO_3$ and containing increased amounts of iron and magnesium.

No detectable amounts of Ni, Co, Pb, Zn and Cu have been estimated by means of the applied analytical methods.

Table 3

Electron microprobe analyses of monocrysts in carbonate concretion from Hieroglyphic Beds (sample *3*)

Point of analysis	Element content in weight per cent				Carbonate content in vol. per cent				Mineral name
	Mn	Fe	Ca	Mg	$MnCO_3$	$FeCO_3$	$CaCO_3$	$MgCO_3$	
1	36.7	1.8	5.3	2.5	72.0	3.2	14.0	10.8	Ca-Mg--rhodochrosite
2	33.2	0.9	9.4	1.6	64.5	2.2	25.8	7.5	Ca-Mg--rhodochrosite
3	1.1	29.9	4.4	8.8	1.9	51.5	10.7	35.9	Ca-pistomesite
4	0.6	31.7	4.0	10.5	0.9	50.9	8.9	39.3	Ca-pistomesite
5	0.3	5.6	28.4	5.3	0.5	9.6	68.6	21.3	Mg-Fe-calcite

FINAL REMARKS

Chemical and mineralogical study of carbonate concretions occurring in Eocene shales in the environs of Dynów indicate that they show variable mineral composition. Concretions from Variegated Shales consist of calcareous rhodochrosite or ponite, whilst those from Hieroglyphis Beds are composed predominantly of sideritic phases accompanied by rhodochrositic ones. Chemical composition of the former correspond to Ca-pistomesite, whilst of the second one — to Ca-Mg-rhodochrosite. Besides, the presence of dipersed grains consisting of Mg-Fe-calcitic phase was discovered by means of electron probe microanalysis. The both principal phases display distinct variations of main components and form disordered intergrowths within the whole mass of the concretions studied. Only locally there occur small, irregular, polycrystalline aggregates showing gradual variation of Mn, Fe and Mg contents whereby Ca concentration remains constant. Iron and magnesium dominate in carbonate phases constituting central parts of these aggregates whilst manganese — in those forming their outer parts.

Similar chemical and mineralogical character of carbonate concretions from Variegated Shales and Hieroglyphic Beds in the Carpathian Flysch was reported by Narębski (1958). Application of modern methods of mineralogical study allowed to find more detailed data on phase composition of these concretions and on internal geochemical variations within them.

REFERENCES

[GABINIET M. P.] ГАБИНЕТ М. П., 1964: К минералогии карбонатных образований верхнеэоценового флиша Советских Карпат. *Минералог. Сб. Львовск. Ун-та.* 18, 1, 104—107.

[GABINIET M. P.] ГАБИНЕТ М. П., 1970: О карбонатах нижнеэоценового флиша Украинских Карпат. В кн.: Вопр. минералогии осадочных образований. 8. Львов, изд-во Львовск. Ун-та.

[GABINIET M. P.] ГАБИНЕТ М. П., 1974: Диагенетические карбонатные конкреции и их распределение во флишевых толщах Украинских Карпат. Геол. и геохимия горючих ископаем. 38.

JOHNS J. B., SANDERS J. V., SEGNIT E. R., 1964: Structure of opal. *Nature* 204, 990—991.

KOTLARCZYK J., 1966: Poziom diatomitowy z warstw krośnieńskich na tle budowy geologicznej jednostki skolskiej w Karpatach polskich. *Studia Geol. Pol.*, 19.

LIPPMANN F., 1973: Sedimentary carbonate minerals. Berlin—Heidelberg—New York.

MOENKE H., 1962: Mineralspektren. Berlin.

NARĘBSKI W., 1958: Mineralogia i geochemiczne warunki genezy tzw. syderytów fliszu karpackiego. *Arch. Miner.* 21. 1.

RAJCHEL J., 1976: Budowa geologiczna rejonu Dynowa—Dubiecka. Doctor thesis. Akad. of Mining and Metall. Cracow.

TOKARSKI A., BADAK J., DZIEWAŃSKI J., GUCIK S., JUCHA S., KOTLARCZYK J., STARKEL L., 1961: Problemy geologiczne jednostki śląskiej, podśląskiej i skolskiej w szerokim otoczeniu Gór Słonych. *Przew. XXXIV Zjazdu PTG.* Warszawa.

Marek MUSZYŃSKI, Jacek RAJCHEL, Witold SALAMON

WĘGLANY ŻELAZA I MANGANU W KONKRECJACH Z ŁUPKÓW EOCEŃSKICH OKOLIC DYNOWA KOŁO PRZEMYŚLA (KARPATY FLISZOWE)

Streszczenie

Przeprowadzono badania składu mineralnego kilku węglanowych konkrecji z łupków eoceńskich jednostki skolskiej. Stosowano obserwacje mikroskopowe, analizę rentgenograficzną, spektroskopową absorpcyjną w podczerwieni oraz chemiczną. Stwierdzono, że konkrecje z pstrych łupków i z warstw hieroglifowych mają odmienny skład mineralny. Pierwsze z nich tworzy wapnisty rodochrozyt lub ponit. W budowie drugich współuczestniczą: Ca-pistomezyt i Ca-Mg-rodochrozyt oraz niekiedy Mg-Fe-kalcyt, tworząc nieuporządkowane przerosty w obrębie całej masy konkrecji. Poszczególne kryształy tych faz cechuje zmienna zawartość podstawowych składników. W mikroobszarze spotykano ponadto lokalnie drobne, polikrystaliczne skupienia, charakteryzujące się zmienną zawartością Mn, Fe i Mg przy stabilnym udziale Ca. Żelazo i magnez dominują w fazach węglanowych z centralnych części tych skupień, natomiast mangan w ich strefach zewnętrznych.

OBJAŚNIENIA FIGUR

Fig. 1. Lokalizacja miejsc pobrania próbek

A — syntetyczny profil litologiczny górnej części pstrych łupków oraz warstw hieroglifowych z okolic Dynowa, *B* — mapa schematyczna, *1—6* numery próbek, *a* — konkrecje węglanowe, *b* — pstre łupki, *c* — piaskowce, *d* — zielone łupki, *e* — zielone rogowce, *f* — margle globigerinowe, *g* — główne nasunięcia

Fig. 2. Dyfraktogramy rentgenowskie węglanowych konkrecji z warstw hieroglifowych (*1, 3, 4*) i pstrych łupków (*6*) okolic Dynowa

R i *S* — refleksy faz zbliżonych odpowiednio do rodochrozytu i do syderytu

Fig. 3. Widma absorpcyjne w podczerwieni węglanowych konkrecji z warstw hieroglifowych (*1—4*) i pstrych łupków (*5, 6*) okolic Dynowa

Fig. 4. Wykresy koncentracji Ca, Mn, Mg i Fe w mikroobszarze węglanowej konkrecji z warstw hieroglifowych (próbka *3*)

Profil półilościowej analizy na MAR przecina zbity agregat polikrystaliczny Mn-węglanu

Fig. 5. Wykresy koncentracji Ca, Mn, Mg i Fe w mikroobszarze węglanowej konkrecji z warstw hieroglifowych (próbka *3*)

Profil półilościowej analizy na MAR przecina typowe wzajemne przerosty kryształów Mn-węglanów i Fe-węglanów

Fig. 6. Wykresy koncentracji Ca, Mn, Mg i Fe w mikroobszarze węglanowej konkrecji z warstw hieroglifowych (próbka *1*)

Lewa część profilu półilościowej analizy na MAR przecina zbite skupienie kryształów, cechujące się stopniowymi zmianami zawartości Fe, Mg i Mn. Spadkowi zawartości Fe i Mg towarzyszy wzrost koncentracji Mn, ilość Ca jest stabilna

Fig. 7. Wykresy koncentracji Ca, Mn, Mg i Fe w mikroobszarze węglanowej konkrecji z warstw hieroglifowych (próbka *1*)

Profil półilościowej analizy na MAR przecina charakterystyczne przerosty faz Mn-węglanów i Fe-węglanów

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Jednorodna, drobnokrystaliczna struktura konkrecji węglanowej z warstw hieroglifowych. 1 nikol. Pow. × 80

Fot. 2. Otwornica aglutynująca o szkieleciku zbudowanym z ziarn kwarcu w konkrecji węglanowej z warstw hieroglifowych. Nikole X. Pow. × 80

Марэк МУШИНЬСКИ, Яцек РАЙХЭЛЬ, Витольд САЛАМОН

КАРБОНАТЫ ЖЕЛЕЗА И МАРГАНЦА В КОНКРЕЦИЯХ ИЗ ЭОЦЕНОВЫХ СЛАНЦЕВ РАЙОНА ДЫНОВА ВБЛИЗИ ПШЕМЫСЛЯ (ФЛИШЕВЫЕ КАРПАТЫ)

Резюме

Были проведены исследования минерального состава нескольких карбонатных конкреций из эоценовых сланцев скольской единицы. Применялись микроскопические наблюдения, рентгенографический, ИК-спектроскопический и химический анализы. Обнаружено, что конкреции из пёстрых сланцев и иероглифических слоёв отличаются минеральным составом. Первые составлены из кальциевого родохрозита или понита.

в строении вторых содействуют: Са-пистомезит и Са-Мg-родохрозит, а иногда Mg-Fe-кальцит, образуя неупорядоченные сростки в массе конкреции. Для одиночных кристаллов этих фаз свойственно изменение содержания основных составных. В микроскопе были видны тоже иногда мелкие, поликристаллические агрегаты, которым свойственна переменчивость содержания Mn, Fe, Mg при постоянном количестве Ca. Железо и магний преобладают в карбонатных фазах из центральных частей этих агрегатов, в то же время марганец в их наружных зонах.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Положение мест отбора образцов

A — синтетический литологический профиль верхней части пёстрых сланцев и иероглифических слоёв из окрестности Дынова: *1—6* — номера образцов, *a* — карбонатные конкреции *b* — пёстрые сланцы, *c* — песчаник, *d* — зелёные сланцы, *e* — зелёный роговик, *f* — глобигериновые мергели, *g* — главные надвиги, *B* — схематическая карта

Фиг. 2. Рентгеновские дифрактограммы карбонатных конкреций из иероглифических слоёв (*1, 3, 4*) и пёстрых сланцев (*6*) из окрестности Дынова. *R* и *S* — рефлексы фаз близких родохрозиту и сидериту

Фиг. 3. ИК-спектры поглощения карбонатных конкреций из иероглифических слоёв (*1—4*) и пёстрых сланцев (*5, 6*) из окрестностей Дынова

Фиг. 4. Графики концентрации Ca, Mn, Mg и Fe в карбонатной конкреции из иероглифических слоёв (образец *3*)

Профиль полуколичественного анализа на MAR пересекает плотный поликристаллический агрегат Mn-карбоната

Фиг. 5. Графики концентраций Ca, Mn, Mg, Fe в поле зрения микроскопа в карбонатной конкреции из иероглифических слоёв (образец *3*)

Профиль полуколичественного анализа на MAR пересекает типичные взаимные прослойки кристаллов Mn-карбонатов и Fe-карбонатов

Фиг. 6. Графики концентраций Ca, Mn, Mg и Fe в карбонатной конкреции из иероглифических слоёв (образец *1*)

Левая часть профиля полуколичественного анализа на MAR пересекает плотный агрегат кристаллов, для которого характерны постепенные изменения содержания Fe, Mg, Mn. Снижению содержания Fe и Mg сопутствует возрастание концентрации Mn, содержание Ca постоянно

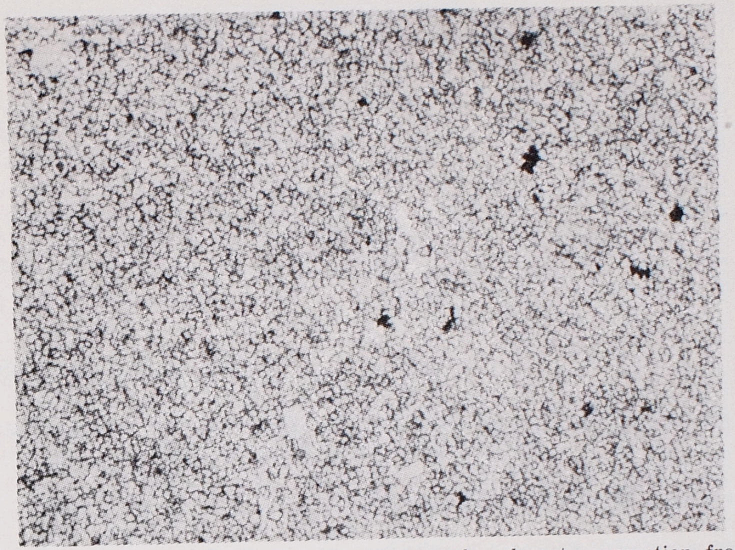
Фиг. 7. Графики концентрации Ca, Mn, Mg и Fe в карбонатной конкреции из иероглифических слоёв (образец *1*)

Профиль полуколичественного анализа на MAR пересекает характеристические сростки фаз Mn-карбонатов и Fe-карбонатов

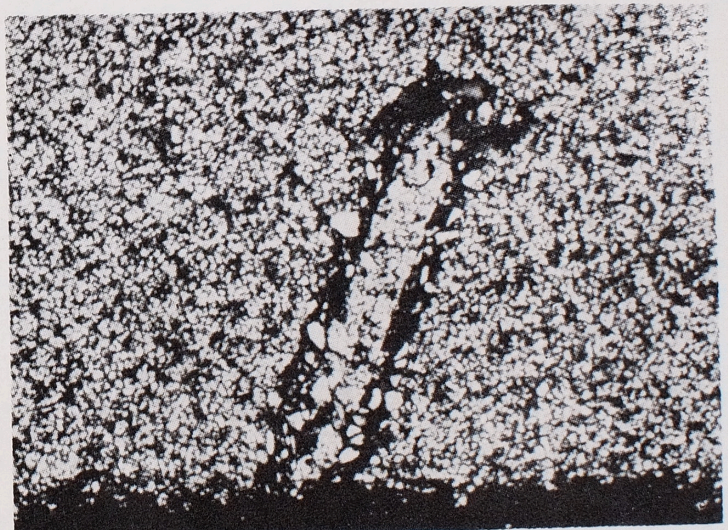
ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото 1. Однородная, мелкокристаллическая структура бикарбонатной конкреции из иероглифических слоёв. 1 николь. Увеличение × 80

Фото 2. Агглютинирующая глобигерина со скелетом построенным из зерн кварца в карбонатной конкреции из иероглифических слоёв. Скрещённые николи. Увеличение × 80



Phot. 1. Homogeneous, fine-crystalline structure of carbonate concretion from Hieroglyphic Beds. 1 nicol. Magn. × 80



Phot. 2. Agglutinated foraminifera with skeleton composed of quartz grains in carbonate concretion from Hieroglyphic Beds. X nicols. Magn. × 80

Marek MUSZYŃSKI, Jacek RAJCHEL, Witold SALAMON — Conctretionary iron and manganese carbonates in Eocene shales of the environs of Dynów near Przemyśl (Flysch Carpathians)