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BIRNESSITE MICRONODULES IN THE POLISH CARPATHIANS FLYSCH DEPOSITS

Abstract. The birnessite micronodules were found in the Polish Carpathians Flysch only in Cenomanian and Turonian gray radiolarian shales and red shales, respectively. They correspond to siliceous oozes and red clays of actual World Ocean. The reported micronodules appear as genetically bound with axial Thetis Ocean currents of cool, oxygen-rich bottom waters, comparable with recent ones, e.g. antarctic (AABW) of the Pacific. Though much less abundant than their manganiferous carbonate equivalents (Wieser, 1982), they show further and more pronounced mineralogical and geochemical features common with the manganese micronodules of recent World Ocean deposits. This is also true in respect to major and minor element composition of particular growth zones of the micronodules. The fresh-water and marine birnessites may be distinguished after the kind of cations occupying interlayer spaces of these phyllomanganates. Mg, K, Ba and Sr ions characteristic for marine birnessites are responsible for contraction of layer-type structure, as indicate c parameter dimensions.

INTRODUCTION

The appearance of fossil deep-sea micronodules on land areas seems to be an extremely rare case. To this statement inclines Jenkyns'a (1977) list of equivalent macronodules embracing only five known occurrences. As far as present author knowledge extends, only one occurrence of micronodules in Cretaceous red clays of Timor Island, described by Molengraaff (1922) and El Wakeel with Riley (1961), could be taken into account in this category of nodules. However, economic reasons prompted exploration by dredging and logging of the oceanic bottom, what led to the discovery of a plenty of manganese macro- and micronodule-bearing horizons. Considering the results of statistic evaluations recorded by Glasby (1978) it may be concluded that practically, they appear in almost all, but invariably oceanic crust--bound sedimentary formations, ranging from Jurassic until Recent times.

In comparison with oceanic manganese macronodules, their counterparts with maximum size arbitrarily chosen at 1 mm. in diameter — micronodules, are much less investigated. This concerns as well their mineral as chemical constitution, though after evaluation made by Chester and Hughes (1969), approximately 85 per cent of hydrogeneous manganese is present in the micronodule fraction.

Birnessite has undergone the strange experience of a mineral which was one day believed to be uncommon one and almost the next day was learned to be one of the

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most abundant minerals. This odd development hinged upon the exactness of X-ray examinations, which at last revealed that a large part of the manganese minerals contained in oceanic nodules was in reality composed of birnessite. The phase δ-MnO_2, another important component, is now frequently considered as a more oxidized, unordered and amorphous member of a single birnessite group of minerals. It is deprived of the majority of X-ray reflections, excluding two lines, namely 2.4 and 1.4 Å. It should be also added that the controversial existence of todorokite in the nodules was at last settled not in favour of buserite and its breakdown products, birnessite and manganite, but in favour of the integrity of todorokite (tectomanganate with multidimensional tunnels, fide Burns et al., 1983). This is not without importance because mentioned birnessite and δ-MnO_2 are subordinate components in regard to todorokite. However, they become, especially the second one, dominant in deposits of seamount vicinity and other, better oxidized and shallower environments, including also near-shore, continental margin environments. Barnes (1967) and Bender (1972) established after Pacific examples that above 3500 m. depth δ-MnO_2 becomes only or dominant constituent, whereas below this depth todorokite and birnessite may be only accompanied by δ-MnO_2.

Birnessite was already reported from deposits of Polish Carpathians Flysch formations as component of ferromanganese macronodules (Gucwa, Wieser, 1978 and Cieszkowski, Wieser, 1979). For instance, in Ostrósza, in Lower Eocene green shales interlayered with Ciężkowice Sandstone (Silesian nappe) occur macronodules composed of todorokite, pyrolusite, goethite, haematite, as well as of birnessite in crustal zone. Another example near Tarnawa Dolna, in lower part of Lower Eocene green and red shales of Magura nappe, birnessite forms either crustal zone or/and peripheral parts of oligonite and Ca-rhodochrosite concretions. In similar geological position were found rhodochrosite macronodules with birnessitic crustal zones in Rdzawka, near Chabówka (Cieszkowski and Wieser, 1979).

GEOLOGICAL MODE OF OCCURRENCE

In almost all tectonic units of the Polish Carpathians green to black synchronic pelagic-type Radiolaria Shales with radiolarites of Cenomanian age are reported. They are comparable with siliceous Radiolaria oozes of the recent World Ocean. Due to the dark brown to black manganese overcrusts and incrustations in their bottom portions being popularly called — Manganiferous Shales, they appear also in investigated deposits of Silesian nappe in Lanckorona village vicinity (30 km. SE of Cracow).

Other than crusts forms of manganese compounds aggregations comprise: 1 — discoidal to ellipsoidal macronodules, up to 8 cm. large, 2 — generally isometric micronodules, up to 1.13 mm. in diameter, 3 — usually a little smaller, rhombohedral, Mn-rich carbonate crystals and their oxidized and hydrated (birnessite) pseudomorphs.

The macronodules and carbonate crystals are practically restricted only to the overlying red shales, constituting lower part (of Turonian age) of Godula Beds. More details, including micropaleontological data and whole profile relates just published by Geroch and Wieser (1983) report.

The lowermost (oldest) samples from Radiolaria Shales (Upper Cenomanian) abound in phosphatized scales and other fish debris, variously replaced by manganese compounds (a.o. manganite). Covering sediments contain first sporadic birnessite micronodules, less frequent fish scales and pyroclastic augite. Then manganese micronodules become more and more numerous with simultaneously changing colouring of shales from dark green-gray into red, marking the transition to next formation.

In red or variegated shales of Godula Beds (Turonian-Lower Senonian), comprising many tens of metres in comparison with few metres measuring radiolarian shales, manganese macro- and micronodules frequent only separated levels. These contain usually abundant authigenic Mn-rich carbonate crystals an/or their pseudomorphs. Manganese micronodules, sometimes with accompanying macronodules are bound with deposits of reduced sedimentation ratio or even with hiatus levels. Here and there, the red colour of sediment may change into greenish, due to local enrichment in organic material giving rise to secondary reduction processes. This may be facilitated by coarser-grained turbiditic, sandy and silty sediments.

MINERALOGICAL FEATURES

Reversely to already recorded (Wieser, 1982) Mn-rich carbonate crystals of authigenic (diagenetic) origin, now presented manganese mineral aggregations, in the shape of micronodules and pseudomorphs after mentioned crystals, are monomineralic. In associated macronodules besides manganese mineral occur: subordinate goethite and rarely — quartz, feldspar and clay minerals. On the contrary, in micronodules if some admixture occurs then it is limited to core and usually served as nucleus. It is constituted by such minerals as quartz, feldspar or phosphate mineral (francolite) fossilizing fish debris, a.o. Sometimes relict rhodochrosite may be present as eventual, rare and small addition.

The individuality of the manganese mineral composing micronodules, authigenic crystal pseudomorphs and partly macronodules discloses already specific megascopic features, like: colour, lustre and streak. The first mentioned property is a little varying according to the origin, namely from dark brown in micronodules to almost black in the pseudomorphs. Correspondingly, the lustre changes from more dull and silky to more pitchy. In macronodules the colour remains distinctly dark brown and the lustre dull and earthy on external surfaces, but on fresh fracture surface it is partly submetallic. The streak is always more or less brown-black.

The specific gravity was determined volumetrically in thin pipe using special liquid medium of high boiling point and low viscosity. The volume changes were measured applying microscope with micrometric ocular. The obtained values did not surpass 2.94 g/c.c. Hardness of manganese mineral amounted — 1.5.

The crystallinity grade of the examined mineral is rather conspicuous, almost submicroscopic, determinable only under electron scanning microscope magnifications. The dimensions of crystallites with platy to lenticular shape were measured on electron micrographs (Phot. 9 and 15). They fluctuated between 2000 Å and 6000 Å. These values significantly exceed those recorded for recent oceanic samples, equaling only 50—100 Å.

The orientation of crystallites is orderless, while stratal arrangement, judging from external shape, may signify the presence of one (monomicronodules, e.g. Phot. 10), two (Phot. 7, 12) or more nuclei (polymicronodules, e.g. Phot. 13 and 14). In the pseudomorphs (Phot. 4—6) the orientation of crystallites is somewhat ordered. Maximum diameter of polymicronodules reaches 1.13 mm. and of pseudomorphs only 0.4 mm., usually ranging between 0.5—0.8 and 0.2—0.4 mm, respectively.

The only certain approch toward the solution of the identity of such as examined manganese mineral may be based on X-ray powder patterns. The results tabulated

Table 1

X-ray data for Lanckorona and other birnessites (natural and synthetic)

Micronodule (average)		Pseudomorph (average)		Macronodule (average)		Birnessite Jones, Milne		Mn-oxyhydroxide Giovanoli et al.		
$d(Å)$	I/I_o	$d(Å)$	I/I_o	$d(Å)$	I/I_o	$d(Å)$	I/I_o	$d(Å)$	I/I_o	hkl
7.26	100	7.32	100	7.18	80	7.27	s	7.21	100	001
3.61	30	3.65	30	3.61	10	3.60	w	3.61	80	002
2.462	20	2.456	30	2.455	20	2.44	m	2.46	100	100
								2.33	100	101
								2.04	80	102
1.804	5	1.781	5					1.802	10	004
								1.723	80	103
								1.454	20	104
1.422	15	1.419	20	1.428	10	1.412	m	1.422	40	111

s — strong line, m — medium l., w — weak l.

above (Table 1) are compared with birnessite described by Jones and Milne (1956) and named after first locality at Birness, Scotland, where occurs in fluvio-glacial deposits. Another comparison was made with synthetic Mn-oxyhydroxide (δ-MnO_2) investigated by Giovanoli et al. (1970). The reflectons for d_{004} are relatively very feeble and variable, what may be deduced from Glower's (1977) data ($d_{004} = 1.775—1.778$ Å). Other reflections cited by Giovanoli et al. (op. cit.) were found to be much diffuse, indeterminable.

The comparison of calculated unit cell parameters a and c for all examined Lanckorona samples with selected examples from Jones and Milne (1956), Giovanoli et al. (1970) and Glover (1977) works implies differences originated by presence of divers additional cations in interlayer spaces:

	a (Å)	c (Å)
Birnessite micronodules, Lanckorona (average)	5.692	14.386
Birnessite macronodules, Lanckorona (average)	5.722	14.433
Birnessite pseudomorphs, Lanckorona (average)	5.700	14.439
Mn-oxyhydroxide (δ-MnO_2), $Mn_7O_{13} \cdot 5H_2O$, Giovanoli et al.	5.688	14.440
Birnessite, $(Na_{0.7}Ca_{0.3})Mn_7O_{14} \cdot 3H_2O$, Scotland, Jones & Milne	5.82	14.62
Birnessite, $(Na_{0.46}Ca_{0.12}K_{0.25}Mg_{1.04})Mn_{5.96}O_{13.6} \cdot 5H_2O$, Gulf of Mexico, Glover (av.)	5.700	14.226

From the above listed parameters especially c values show distinct disparities caused by nonuniform packing of MnO_6-octahedron layers. The parameter c makes evident the space between the main layers (~ 7 Å) of MnO_6-octahedrons with stacking corresponding to orthorhombic supra-cell and hexagonal sub-cell. In marine birnessites from Gulf of Mexico this space is markedly contracted due to the presence of Mg^{2+} and K^+ ions, particularly if one compares it with that of fluvio-glacial, Na^+—and Ca^{2+}—rich birnessites. Among the Lanckorona birnessites those composing pseudomorphs demonstrate higher c-values than those constituting micronodules. This rests in accordance with various modes of crystallization (by replace-

ment or precipitation from pure solutions) and probably with differences in accretion ratio, redeposition etc. The existence of Mg, Ba and Sr ions, stabilizing and contracting factor in the structure of reported phyllomanganate, was confirmed by the semi-quantitative emission-spectral analyses (for results see next chapter).

Further data concerning the structure of discussed mineral yield infra-red absorption spectra. After Potter's and Rossman's (1979) opinion infra-red spectra of natural and synthetic birnessites exhibit various band position and to a larger extent changing relative band intensity. Nevertheless, the general similarity of the spectra points out the same basic layer structure (c.f. positions of the major bands in the 1400 to 200 cm^{-1} region). The absorption maximum near 3400 cm^{-1} (see Fig. 1) is interpreted by mentioned authors as produced by hydroxyl ions in a specific structural site, while less ordered water is responsible for remaining bands in the 4000 to 1400 cm^{-1} region. Birnessites can be discerned from most of the manganese oxide minerals by two broad extrema differently situated in vicinity of 460 cm^{-1} and 510 cm^{-1} wave numbers. The relatively low sharpness of the peaks (Fig. 1) in majority of natural birnessites in comparison with synthetic ones visualizes low crystallinity grade and structural ordering of material. Potter and Rossman (1979) reject Chukhrov's et al. conclusion (1978 a, b; fide Potter and Rossman, op. cit.) that birnessite and vernadite (δ-MnO_2) can be distinguished after IR spectra. They argue their assumption by the statement that corresponding 510 versus 500 cm^{-1} and 470 versus 435 cm^{-1} bands fall within the variation in the spectra of their birnessite samples. This is a striking example how identification of a mineral hinges upon interpretation of analytical data.

GEOCHEMICAL FEATURES

Small quantity of available material caused that only semi-quantitative emission-spectral analyses and X-ray micro-probe analyses were performed.

Spectrochemically determined major and minor element content in birnessite micronodules is relatively uniform, averaging as follows (in per cents): Fe — 2,
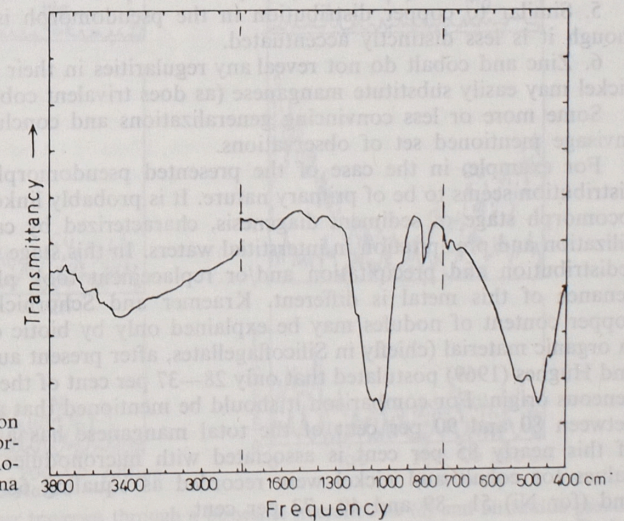

Fig. 1. Infra-red absorption spectrum of birnessite forming micro- and macronodules in the Lanckorona occurrence

Mg — 3, Al — 0.5, Ca — 0.1, Ba — 1, Sr — 0.1, Ni — 0.5, Cu — 0.2. Simultaneously analysed macronodules are characteristically Fe-richer and Mn- and Mg-armer, and do not reveal substantial enrichment in trace elements in relation to micronodules.

Other important data regarding distribution of major and minor elements were received applying X-ray micro-probe analyses with X-ray microanalyser CAMECA MS 46. They were executed on more or less diagonal or equatorial sections of micronodule (a) and pseudomorph (b) after authigenic Mn-rich carbonate crystal (b). This way, the traverses carried out in directions and at distances demonstrated on Fig. 2 allowed to cross as well inner (core) as outer (peripheral and crustal) zones.

The registered fluctuations in major and minor element pairs disclose some regularities, which can be expressed as follows:

1. Iron and manganese remain in micronodule (a) and pseudomorph (b) in antipathetic relations. Iron is a little enriched in core and in crustal part. The last one, goethite-rich, may be fragmentarily lost due to secondary mechanical erosion or solution. Calvert and Price (1970) interpreted this phenomenon in terms of occurrence of the micronodules with ferruginous rims near or on sediment surface, while those from about 10 cm depth are deprived of such crusts. It is also reasonable here to mention, that Addy (1978) observed another interesting dependence: the smaller the micronodules the lower are their Mn/Fe ratio, what can be accounted for by incipient iron oxyhydroxide layers on micronodule nuclei.

2. Calcium and barium show more distinct negative correlation in pseudomorph than in the micronodule example. This is in accordance with known small extent of substitution of Ca by Ba and Sr in calcium carbonate minerals (possible especially in aragonite).

3. There are faintly marked symptoms of magnesium enrichment confined to the core, what infers probable derivation from mafitic pyroclast nuclei.

4. The distribution of copper content is more peculiar for pseudomorphs, where it is very distinctly rising toward peripheries. Well visible positive correlation of copper with calcium was already emphasized by Calvert and Price (1970).

5. Similar to copper distribution in the pseudomorph is the nickel partition, though it is less distinctly accentuated.

6. Zinc and cobalt do not reveal any regularities in their distribution; they like nickel may easily substitute manganese (as does trivalent cobalt in respect to iron).

Some more or less convincing generalizations and conclusions arise when one envisage mentioned set of observations.

For example, in the case of the presented pseudomorph (b) calcium content distribution seems to be of primary nature. It is probably linked with later, so-called locomorph stage of sediment diagenesis, characterized by calcium carbonate mobilization and precipitation in interstitial waters. In this stage simultaneously copper redistribution and precipitation and/or replacement took place, though the provenance of this metal is different. Kraemer and Schornick (1974) noticed that copper content of nodules may be explained only by biotic contribution, included in organic material (chiefly in Silicoflagellates, after present author remark). Chester and Hughes (1969) postulated that only 28—37 per cent of the total Cu has a hydrogeneous origin. For comparison it should be mentioned that after the same authors between 80 and 90 per cent of the total manganese has a hydrogeneous origin, of this nearly 85 per cent is associated with micronodules, while corresponding values for cobalt and nickel were recorded as equaling 68—98 and 95 per cent and (for Ni) 51—89 and 40—72 per cent.
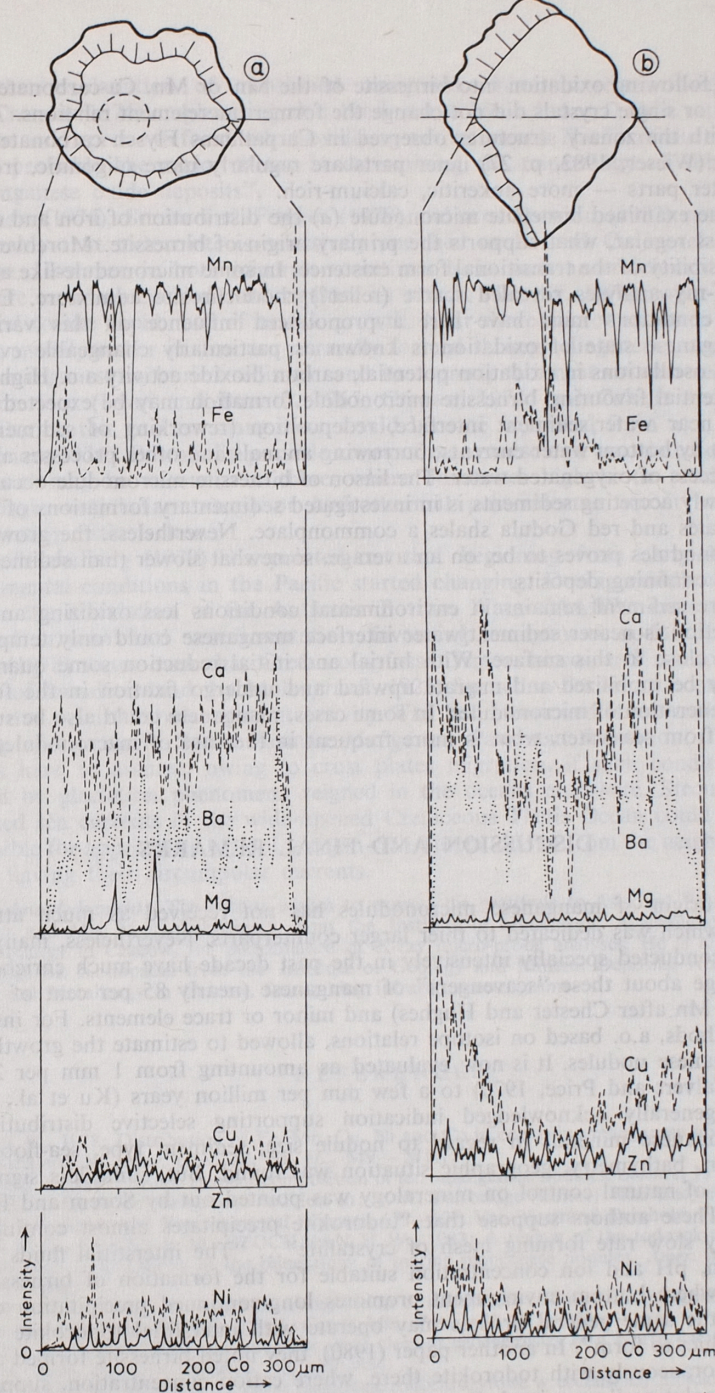
Fig. 2. X-ray microanalyser traverses through a birnessite micronodule (a) and birnessitic pseudomorph (b) after diagenetic calciferous rhodochrosite crystal, from Lanckorona occurrence. Dashed line in the micronodule section denotes its real central part. Further explanations in text

The following oxidation into birnessite of the Mn or Mn, Ca-carbonate micronodules or single crystals did not change the former interelement relations. Accordingly with the zonary structures observed in Carpathians Flysch carbonate micronodules (Wieser, 1982, p. 27) inner parts are regularly more oligonitic, iron-rich, and outer parts — more ankeritic, calcium-rich.

In the examined birnessite micronodule (a) the distribution of iron and calcium is far less regular, what supports the primary origin of birnessite. Moreover, there is a possibility of the transitional form existence. In some micronodule-like aggregations X-ray analyses revealed scarce (relict?) rhodochrosite admixture. Environmental conditions must have here a pronounced influence on this variability.

Manganese state of oxidation is known as particularly changeable even due to small oscillations in oxidation potential, carbon dioxide activity a.o. High oxidation potential favouring birnessite micronodule formation may be expected during growth near water/sediment interface, redeposition (reworking of sediment with nodules) by bottom water currents, burrowing animals and other processes allowing better access of oxygenated water. The liason of birnessite micronodule occurrences with slowly accreting sediments is in investigated sedimentary formations of Radiolaria Shales and red Godula shales a commonplace. Nevertheless, the growth rate of micronodules proves to be, on an average, somewhat slower than sedimentation ratio of confining deposits.

Where sediment remains in environmental conditions less oxidizing and zone of reduction is nearer sediment/water interface manganese could only temporarily be fixed close to this surface. With burial and initial reduction some quantity of Mn may be mobilized and migrate upward and undergo fixation in the form of a new generation of micronodules. In some cases, manganese could also be supplied directly from sea-water, what is more frequent in the case of macronodules.

DISCUSSION AND FINAL REMARKS

The origin of manganese micronodules has not received as much attention as that which was dedicated to thier larger counterparts. Nevertheless, many-sided studies conducted specially intensively in the past decade have much enriched our knowledge about these "scavengers" of manganese (nearly 85 per cent of hydrogeneous Mn after Chester and Hughes) and minor or trace elements. For instance, new methods, a.o. based on isotope relations, allowed to estimate the growth ratio of manganese nodules. It is now evaluated as amounting from 1 mm per 25—60 years (Calvert and Price, 1970) to a few mm per million years (Ku et al., 1979).

No generally acknowledged indication supporting selective distribution of ferromanganese minerals in regard to nodule size, sediment type, sea-floor configuration, bathymetry, geographic situation was found. But, some less significant evidence of natural control on mineralogy was pointed out by Sorem and Fewkes (1979). These authors suppose that "todorokite precipitates almost continuously at a very slow rate forming mesh of crystallite"... "The interstitial fluids finally reach Eh, pH and ion concentration suitable for the formation of birnessite. In regions where bottom environment promotes long-continued precipitation of birnessite, the same general process may operate with interstitial todorokite as the last product to form". In another paper (1980), they noted birnessite formed almost contemporaneously with todorokite there, where cation concentration, supposedly in "rest-solutions" permitted.

Another explanation of mentioned manganese minerals relation suggested earlier Cronan (1974) emphasizing that "todorokite has a lower O: Mn ratio than birnessite and is prone to form in less-oxidizing environments. The Eh of the environment is probably the major factor in determining the mineralogy of submarine ferromanganese oxide deposits".

Cronan (1974), Sorem and Fewkes (1979) and a.o. Ostwald (1982) postulated conformably that todorokite is selectively enriched in Ni and Cu in relation to birnessite. However, in both minerals sometimes lacks such an enrichment within near-shore environment sediment against its matrix (Glasby, 1978), what can be attributed to the rapid rate of nodule growth. Near-shore micro- and even macronodules, usually richer in iron are normally formed through diagenetic remobilization of manganese in buried sediment and its reprecipitation at or near sediment/water interface (Lynn and Bonatti, 1965, Cronan, 1974, and Calvert and Price, 1970). During this process manganese would become separated from a.o. Ni and Cu (Cronan, 1974). Potentially possible zones of manganese and associated elements enrichment may be encountered there, where dominates high biotic productivity (c.f. pelagic radiolarian oozes) or hydrothermal post-volcanic activity and the sedimentation ratio is low.

Von Stackelberg (1979) has pointed out that beginning from early Miocene environmental conditions in the Pacific started changing. During middle and late Miocene the circulation of the Antarctic Bottom Water (AABW) increased and produced erosion and resedimentation favouring manganese nodule creation. Glasby (1978) states even that Cretaceous fossil Timor micro- and macronodules (as first of found on land, by Molengraaff, 1922) formed under similar conditions, that is, due to circumpolar current activity. The last mentioned is the main factor deciding of e.g. recent South Tasman Manganese Pavement formation.

It is hard to assume, owing to crust plates migration, if such conditions influenced by glaciation phenomena reigned in the oceans elsewhere. Strong, wind promoted sea currents in the wide-opened Cretaceous Thetis Ocean could also be responsible for appearance of cool, oxygen-rich waters, driven from the neighbouring oceans having their circumpolar currents.

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Tadeusz WIESER

MIKROKONKRECJE BIRNESSYTOWE W OSADACH POLSKICH KARPAT FLISZOWYCH

Streszczenie

Mikrokonkrecje birnessytowe zostały znalezione w szarych łupkach radiolariowych cenomanu i szczególnie w nadległych czerwonych łupkach godulskich dolnego turonu w okolicach Lanckorony.

Cechami mineralogicznymi i geochemicznymi odpowiadają one obecnie powstającym mikrokonkrecjom todorokitowo-birnessytowym Wszechoceanu. Między innymi, podobieństwa dotyczą także rozmieszczenia pierwiastków Mn, Fe, Ca, Cu i in. w obrębie różnych części mikrokonkrecji.

Obok pierwotnych mono- i polimikrokonkrecji birnessytowych stwierdzono także obecność pseudomorfoz birnessytowych po kryształach i ich mikrokonkrecyj-

nych skupieniach diagenetycznych, złożonych pierwotnie z wapnistego rodochrozytu. O ich obecności sygnalizowano już wcześniej (Wieser, 1982).

Oznaczenia rentgenostrukturalne wykazały przynależność badanego birnessytu z fliszu karpackiego do odmiany cechującej się zmniejszonym parametrem komórki jednostkowej c, typowym dla morskich odmian tego minerału. Związane jest to z kontrakcją struktury wskutek rozmieszczenia w przestrzeniach międzywarstwowych silnie przeważających jonów Mg, K, Ba i Sr.

OBJAŚNIENIA FIGUR

Fig. 1. Widmo absorpcyjne w podczerwieni birnessytu tworzącego makro- i mikrokonkrecje w występowaniu w Lanckoronie

Fig. 2. Trawersy mikroanalizatorem rentgenowskim pzez mikrokonkrecję birnessytu (a) i birnessytową pseudomorfozę (b) po diagenetycznym krysztale wapnistego rodochrozytu; z występowania w Lanckoronie. Linia przerywana na przekroju mikrokonkrecji oznacza jej właściwą część środkową. Dalsze objaśnienia w tekście

OBJAŚNIENIA FOTOGRAFII

Fot. 1—2. Obrazy diagenetycznego Ca-rodochrozytu tworzącego kryształy romboedryczne, w elektronowym mikroskopie skaningowym; okazy z dolnoturońskich czerwonych łupków godulskich z występowania w Lanckoronie. Pow. ×124 i 110, odpowiednio

Fot. 3. Obraz powierzchni kryształu Ca-rodochrozytu (fot. 2) w elektronowym mikroskopie skaningowym. Pow. ×1140

Fot. 4—6. Obrazy pseudomorfoz birnessytowych po kryształach diagenetycznego Ca-rodochrozytu w elektronowym mikroskopie skaningowym, jak pokazanych na fot. 2—1. Dolnoturońskie czerwone łupki godulskie. Występowanie w Lanckoronie. Pow. ×135, 100 i 130, odp.

Fot. 7, 8, 10 i 11. Obrazy dużych mono- i polimikrokonkrecji birnessytowych w elektronowym mikroskopie skaningowym. *Ibidem.* Pow. ×47, 62, 55 i 70, odp.

Fot. 9. Obraz powierzchni jednej z dużych polimikrokonkrecji (fot. 7) w elektronowym mikroskopie skaningowym. Widoczne łuskowe do płytkowych suindywidua (krystality). Pow.— ×1140

Fot. 12—14. Obrazy małych polimikrokonkrecji birnessytowych w elektronowym mikroskopie skaningowym. *Ibidem.* Pow. ×115, 100 i 92, odp.

Fot. 15. Powierzchnia małej polimikrokonkrecji (fot. 14). Pow. ×912

Тадеуш ВИЗЕР

БЁРНЕССИТОВЫЕ МИКРОКОНКРЕЦИИ В ОТЛОЖЕНИЯХ ПОЛЬСКИХ ФЛИШЕВЫХ КАРПАТ

Резюме

Бёрнесситовые микроконкреции были найдены в серых радиоляриевых сланцах сеномана, в частности в вышележащих красноцветных годульских сланцах нижнего турона в окрестностях Лянцкороны.

По минералогическим и геохимическим признакам они соответствуют современно образующимся тодорокит-бёрнесситовым микроконкрециям Мирового океана. Между прочим, сходство обнаруживается также в размещении химических элементов как Mn, Fe, Ca, Cu и других в пределах разных участков микроконкреций.

Кроме первичных бёрнесситовых моно- и полимикроконкреций, обнаружено также присутствие бёрнесситовых псевдоморфоз по кристаллам и их микрожелваковым диагенетическим скоплениям, первоначально сложенных известковым родохрозитом. Об их присутствии упоминалось уже раньше (Wieser, 1982).

Рентгеноструктурными исследованиями обнаружена принадлежность изучаемого бёрнессита из карпатского флиша к модификации, характеризующейся уменьшенным параметром элементарной ячейки c — типичным для морских разновидностей этого минерала. Это связано с контракцией структуры из-за расположения в межпакетных пространствах сильно преобладающих понов Mg, K, Ba и Sr.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. ИК-спектры поглощения бёрнессита, образующего макро- и микроконкреции в местонахождении Лянцкорона

Фиг. 2. Концентрационные кривые микроконкреции бёрнессита (a) и бёрнесситовой псевдоморфозы по диагенетическому кристаллу известкого родохрозита (b) из местонахождения Лянцкорона. Прерывистой линией на разрезе микроконкреции обозначена ее собственно центральная часть. Остальные объяснения в тексте

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото 1—2. Изображение в электронном сканирующем микроскопе диагенетического Са-родохрозита, образующего ромбоэдрические кристаллы, образцы из красноцветных годульских сланцев нижнего турона из местонахождения Лянцкорона. Увел. ×124 и 110 соответственно

Фото 3. Изображение в электронном сканирующем микроскопе поверхности кристалла Са-родохрозита (фото 2). Увел. ×1140

Фото 4—6. Электронно-микроскопические изображения бёрнесситовых псевдоморфоз по кристаллам диагенетического Са-родохрозита (смотри фиг. 1—2). Красноцветные годульские сланцы нижнего турона из местоположения в Лянцкороне. Увел. ×135, 100 и 130 соответственно

Фото 7, 8, 10 и 11. Электронно-микроскопические изображения крупных бёрнесситовых моно- и полимикроконкреций. Там же. Увел. ×47, 62, 55 и 70 соответственно

Фото 9. Электронно-микроскопическое изображение одной из крупных полимикроконкреций (фото 7). Заметны чещуйчатые до пластинчатых субиндивиды (кристаллиты). Увел. ×1140

Фото 12—14. Электронно-микроскопические изображения небольших бёрнесситовых полимикроконкреций. Там же. Увел. ×115, 100 и 92 соответственно

Фото 15. Поверхность небольшой полимикроконкреции (фото 14). Увел. ×912

EXPLANATION OF PLATE

Phot. 1—2. Scanning electron micrographs of diagenetic Ca-rhodochrosite forming rhombohedral crystals; from Lower Turonian Godula red shales in Lanckorona occurrence. Magn. ×124 and ×110, respectively.

Phot. 3. Scanning electron micrograph of Ca-rhodochrosite crystal (Phot. 2) surface. Visible rhombohedric symmetry of etched subindividuals. Magn. ×1140
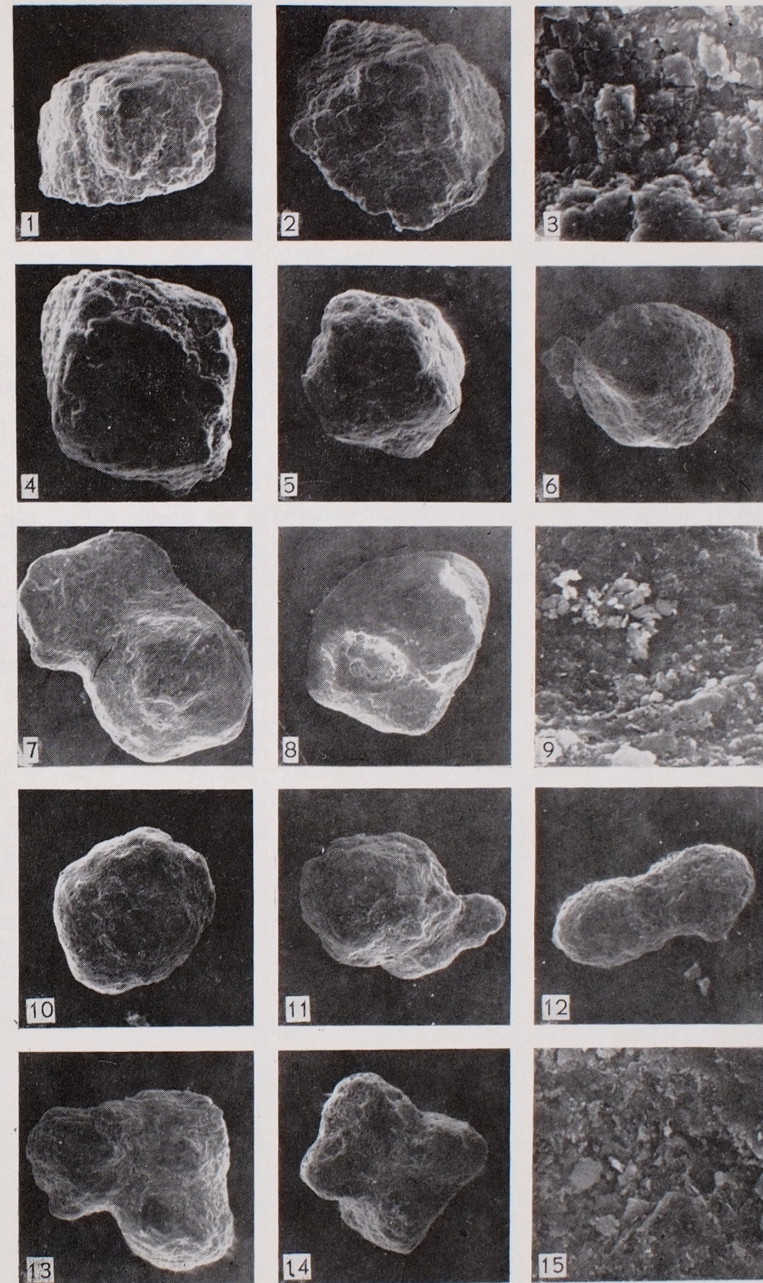
Phot. 4—6. Scanning electron micrographs of birnessite pseudomorphs after diagenetic Ca-rhodochrosite crystals, like shown in Phot. 1—2. Lower Turonian Godula red shales. Lanckorona occurrence. Magn. ×135, 100 and 130 resp.

Phot. 7, 8, 10 and 11. Scanning electron micrographs of large birnessite mono- and polymicronodules. Ibidem. Magn. ×47, 62, 55 and 70, resp.

Phot. 9. Surface of one (Phot. 7) of large birnessite polymicronodule. Discernable flaky or platy subindividuals (crystallites). Magn. ×1140

Phot. 12—14. Scanning electron micrographs of small birnessite polymicronodules. Ibidem. Magn. ×115, 100 and 92, resp.

Phot. 15. Surface of a small polymicronodule (Phot. 14). Magn. ×912

Tadeusz WIESER — Birnessite micronodules in the Polish Carpathians Flysch deposits