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ORIGIN OF REALGAR IN THE FLYSCH DEPOSITS OF THE ENVIRONS OF BALIGRÓD (MIDDLE CARPATHIANS)

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Abstract. The paper deals with the origin of realgar occurring in fissures of the Eocene shales and silicified Hieroglyphic sandstones. In the present writer's opinion this mineral was deposited from alkaline polysulphide solutions originated from the basement underlying the Flysch formation. The presence of the latter is documented by the occurrence of exotic granite, mica schist and amphibolite pebbles within the Oligocene Krosno sandstones. Polysulphide solutions in question are supposed to represent a final stage of epimagmatic phenomena in the above crystalline rocks or to be the products of leaching of primary mineral veins by Flysch saline waters. When permeating through the Flysch deposits these solutions were partly oxidized in hypergenic zone by manganese oxides occurring as incrustations in fissures of the above deposits and as pseudomorphoses after manganese-bearing sphaerosiderites. The presence of heavy metal ions in these polysulphide solutions is manifested by the occurrence of traces of sphalerite within the deposit in question and the distribution of copper ores in variegated shales of the environs of Załuż and Monasterzec. Traces of mercury and cinnabar reported in some publications of 17th century (Jonston, Rzączyński) can also be of the same origin.

The occurrence of realgar in the environs of village Rabe (S from Baligród) was reported first by Kamiński (1937). Rather primitive exploring of this „deposit” was initiated for balneological purposes by dr T. Spitzer who also started to investigate other mineralization phenomena in Middle Carpathians as these of copper minerals in Monasterzec, pyrite in Bezmiechowa, diatom-earth near Ulucz etc. During these works the present writer, being asked to evaluate these „depcsites”, collected some informations concerning their origin.

In agreement with Kamiński's observations, realgar veinlets, up to 3 cm thick, are contained mainly in dark shales whereas the fissures in question are of tectonical origin. As follows from Kamiński's examina-

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tions no arsenic is present in shales. Thus the origin of the above mineral by lateral secretion must be excluded. Moreover Kamiński observed the appearance of realgar crystals within sandstones intercalations in shales. The largest concentrations of coarse-grained realgar were found after the Second World War just in these sandstones when artificial outcrops by the road to Rabe was made. These sandstones had to be primarily porous and later strongly silicified. They contain not only regenerated quartz grains but also secondary coarse-grained quartz cement. Moreover in fissures we observe well-developed short-prismatic quartz crystals called „Marmaros (or Bristol) diamonds” or dragomites. Aggregates of these crystals are usually more compact along lamines observed at the surfaces of these fissures.

Beyond the zone of realgar occurrence the dark shales include fine-grained sandstone intercalations displaying dark banding and calcareous cement. These are developed as typical rocks of the Eocene Hieroglyphic Beds. The walls of fissures of these sandstones are covered with asphaltic matter, underlying quartz crystals and colourized by the former in brown and red. Nevertheless in general these fissures are filled with white or transparent calcite. After dissolving this carbonate we observe some asphaltic plates and very fine quartz crystals displaying euhedral habit with well developed rhombohedral *r* and *z* faces. They were deposited from unquestionably alkaline solutions simultaneously with calcite, whereas the quantitative ratio of these minerals (calcite : quartz) approached the value 2.85 : 0.03. No euhedral calcite grains were found which could be suitable for morphogenetic studies on the influence of As ions from the adjacent deposit on the habit of calcite crystals.

Moreover there occur thin incrustations of iron ochre. It is yellow, yellowish-brown or light red in colour when containing realgar admixture. Light red illinitations on the surfaces of fissures in black shales are known not only in the environs of Baligród but also in those occurring E from Tuchla. As follows from Kamiński's observations, realgar crystals when heated in hand disintegrate due to internal stresses caused probably by anisotropic thermal expansion. No investigations were performed on eventual dependence of these decrepitation phenomena with the presence of liquid or gaseous inclusions.

In an unpublished paper, deposited in the Archive of the Geological Institute in Warsaw, Ostrowicki reports the occurrence of traces of sphalerite in the realgar deposit under consideration. Among other minerals of this paragenesis minute amounts of orpiment were reported by Kamiński. It is well known that cinnabar and native mercury are the most typical minerals depositing from polysulphide solutions. They were not found actually but their presence in the Polish Carpathians was reported in 17th century by Jan Jonston born at Szamotuły (Jonston 1633) and in more detail by Rzączyński in 18th century (Rzączyński 1721). Following informations on this subject are contained in the latter's paper:

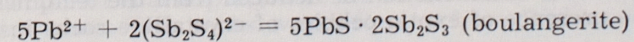
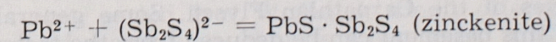
„In monte Zimna Woda sex a Cracovia miliaribus certis anni temporibus ad superficiem terrae sponte erumpit et circa Joannis Baptistae festum, multis illius grana pisorum instar, in radicibus graminum, se collegisse testatur author Tyrocinii

Chymicu 1.2., a Reinzer in Meteorolog. citatus. Mons inter pagos Tarnawa et Rybie, eundem naturae operatricis vi separatum Mercurium habere traditur a Pharmacopolis Cracoviensibus. Idem fert fama contigere in montibus vicinioribus Baligród oppido Palati. Russiae, in quibus, guttatim sparsus assumitur. Eruitur in Russia apud Tustanum, Cromero Poloniae 1.1 teste. Ultra Cracoviam, in Monte Babiagora, atq. in Carpato reperitur. Ilcusii e plumbo, vi ignis evocatur.” (In the Zimna Woda Mts., six miles from Cracow [most probably in connection with andesites occurring near Zegocina — A. Gawel] it erupts to the surface of the Earth. Moreover the author of Tyrocinium Chymicum stated that close to St. John's Baptist's day he collected pellets from the roots of grass. Cracovian pharmacutists report that the mountains between Tarnawa and Rybie [the environs of Zegocina — A. Gawel] contain mercury, produced by creative forces of the nature. There are informations that this metal also occurs in the mountains near Baligród, a Ruthenian district town, where it is dispersed in droplets. According to Cromer (Polonia vol. 1) it is exploited in Ruthenia near Tustan. It also occurs behind Cracow in Babia Góra and in the Carpathians).

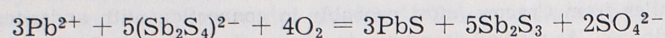
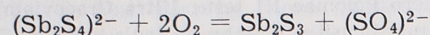
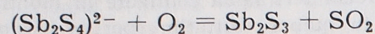
According to the present writer's opinion the latter occurrence refers to the environs of Osielec or to the Pieniny Mts. It should be mentioned that the occurrence of mercury in the latter range was known to Lill de Lilienbach (1830), Austrian geologist and director of the salt mines in Wieliczka. Its presence among ore minerals of Jarmuta (Pieniny Mts.) was stated analytically by Wojciechowski (1950).

These observations and data of the above naturalists were confirmed by Merlich's discovery of cinnabar in the Transcarpathian Russia (*vide* Lazarenko 1957). According to Polish mineralogist Piotrowski (1958, 1961) this mineral was deposited from polysulphide solutions. As follows from this author's experiments HgS may be precipitated from basic aqueous Na₂HgS₂ solution by dilution with water or by oxidation of saturated solution on air or by treating them with hydrogen peroxide.

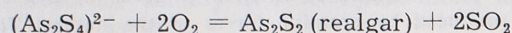
To explain the origin of realgar in the environs of Baligród we may similarly assume the activity of ascending alkaline solutions and their decomposition into constituents, among which only AsS appeared at the surface of the Earth. Intense silification of Flysch sandstones in the region of occurrence of arsenic minerals indicates alkaline character of these solutions. Their neutralization was not possible because of lack of CO₂-bearing rocks in this region. Polysulphide solutions, originated most probably from the crystalline basement of the Carpathians, would be diluted by waters contained in Flysch rocks before their contact with descending waters. Consequently arsenic mineralization would not be near-surface in type. Thus oxidation of polysulphide solutions seems to be most probable. This hypothesis was accepted by Grigoryan (1960) to explain the paragenesis of antimonite and galena. Following Fersman's theory this author assumes the existence of (Sb₂S₄)²⁻ ion being easily soluble when combined with alkalies and neutralized by heavy metal ions as Pb²⁺ in zinckenite and boulangerite or Cu e.g. in tetrahedrite:



According to Grigoryan the oxidation of $(\text{Sb}_2\text{S}_4)^{2-}$ ion results in the formation of antimonite:

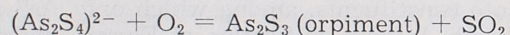
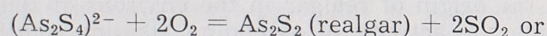


The behaviour of more mobile thioarsenite ion is supposed to be similar:



In the case of realgar occurring in Flysch deposits near Baligród the oxidizing agent had to be one of the components of these rocks. It should be emphasized that dark Cretaceous and Oligocene shales of this area and especially those of the Cisna fold zone distinguish by the presence of manganic oxide illinitations, whereas dark colouration of shales of the Silesian Carpathians is due exclusively to carbonaceous matter dispersed in them. The problem of Mn-enrichment in deeper-water deposits of the Carpathian Flysch in Roumania was examined by Savul et al. (1963 a, b). Generally this element occurs as isomorphic admixture in carbonate concretions (Kuźniar 1932, Kuźniar & Krajewski 1933, Hempel 1933, Narebski 1957). Its enrichment in ashes left after burning petroleum from southern parts of the Middle Carpathians was shown by Złotnicka (1960).

It is thus supposed that Mn^{3+} and Mn^{4+} oxides occurring as illinitations in Flysch rocks of the Eastern Silesian (Cisna) facies played considerable role in oxidation of alkaline polysulphide heavy-metal-bearing solutions. This oxidation can be illustrated by following reactions:



Thus the origin of orpiment admixture is connected with periods of lower oxidizing potential e.g. when only atmospheric oxygen was acting.

Oxidizing action of solid MnO_2 can be demonstrated by simple experiment. Colourless ammonium sulphide solution when treated with a little manganic oxide slowly changes its colour to yellow. This change consists in partial oxidation of sulphide into sulphite or sulphate, whereas the latter decomposes the sulphide ion and the liberated sulphur dissolves in the excess of $(\text{NH}_4)_2\text{S}$ causing gradual development of yellow colouration.

Kamiński was the first to assign the origin of polysulphide solutions with a deeper-seated, most probably crystalline basement underlying the folded series of the Carpathian Flysch. Some general idea on the morphology of this basement can be deduced from the tectonics of Flysch deposits, the presence of exotic pebbles of crystalline rocks in the Flysch

deposits and the area of occurrence of copper, arsenic and other minerals.

Elongated central morphological depression in the eastern part of the Polish Carpathians results from erosion of generally loose Oligocene Krosno sandstones. This zone is limited from south and north by folds and overthrusts consisting of rocks representing all the stratigraphic members of the Flysch series from Cretaceous to Oligocene. The central depression consists of folded Krosno sandstones forming several parallel anticlines having no older beds in their cores. Shallow petroleum shafts were formerly localized on the crests of some of these anticlines e.g. the Zahutyń — Płowce — Pissarowce one. They exploited petroleum-bearing horizon in the Lower Krosno Beds.

Such tectonical development of the Flysch series must reflect the structure of the basement. It is thus supposed that older, pre-Carpathian rock series is also depressed under the area in question.

Paleogeographic and petrographic characteristics of this basement can be deduced basing on detailed study of pebbles occurring nearly in all the stratigraphic members of the Carpathian Flysch. Their geographic and stratigraphic distribution allow to distinguish petrographic provinces of source areas delivering detritic material to the Carpathian geosyncline. So for example during the Cretaceous the northern shore of pre-Carpathian depression consisted of an emerged cordillera and the eroded area was composed of Jurassic limestones and Carboniferous sedimentary rocks. Among pebbles of igneous rocks occurring in Cretaceous Flysch Beds of this region the most interesting are scarce fragments of alkali diabase displaying the same texture and mineral composition as that described by Siegel (1951) from Cretaceous deposits in Lusina, S of Cracow. Chemical analysis and petrographic description given by this author are one of very few characteristics of basic effusive rocks occurring as pebbles in the Carpathian Flysch.

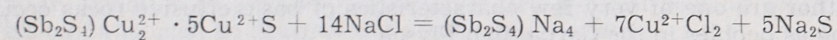
During Cretaceous and Eocene a deepening of the Carpathian sea took place and mainly siderite-bearing shales were deposited whilst in Oligocene a general shallowing was noted. During that period a strongly eroded northern cordillera already consisted of crystalline rocks, which are represented by granite, quartz porphyry, granophyre, gneiss and marble pebbles, forming an „exotic horizon” in the Lower Krosno Beds (Gawel 1931, 1932).

It should be added that already in the Cretaceous the northern part of this cordillera or some other more northern cordilleras furnished granite-gneiss pebbles (the environs of Dębica and Ropczyce) while more eastwards they are accompanied by fragments of greenschists of the Dobruja type or of Riphean rocks occurring *in situ* at the depths of 800—900 m along the Vistula valley between Niepołomice and the mouth of San river.

Because of lack of exotic pebbles, until recently there were no data on the character of the southern margin or the Carpathian geosyncline. During the interwar period Prof. W. Rogala kindly offered to the present writer a sample of coarse-platy chlorite schist found in Cretaceous rocks of the Cisna zone. This rocks was different from Riphean greenschists

and from pebbles occurring in the Truskawiec conglomerats described by Kreutz and Gawel (1926) but it resembled rather chlorite schists occurring as intercalations in amphibolite series or in slipping zones. This opinion was confirmed by the presence of amphibolites among exotic pebbles from the Krosno Beds near Bukowiec (Ślaczka 1961, Ślaczka & Wieser 1962). This suggests that at the southern margin of the Carpathian trough there existed in that time an eroded cordillera consisting of crystalline rocks and metamorphic mantle. It is supposed that the northern part of this cordillera would represent a strongly tectonized zone displaying flexural or even overthrust structure. In this case the occurrence of fissures and mineral veins would be a natural consequence of pre-Carpathian deep-seated tectonics. Amphibolite series of tectonically disturbed massifs generally include ore veins containing quartz, barite, ankerite as well as tetrahedrites, chalcopryrite etc. The region of occurrence of such pre-Carpathian veins is supposed to be the source of solutions, from which the sulphides found in the overlying younger Carpathian Flysch rocks were deposited. These solutions could represent a final stage of post-magmatic hydrothermal phenomena rejuvenated by tectonic movements of the basement during the Cretaceous period when variegated Gcdula shales were deposited.

We may assume that the activity of sea water and especially of more concentrated Flysch salt-waters on sulphides and polysulphides occurring in ore veins of the basement rocks resulted in their decomposition and mobilization. As follows from Nesterova's (1960) investigations a part of copper contained in tetrahedrites can be comparatively easily mobilized. Under ideal conditions this reaction may proceed as follows:



Thus initiated long-range migration of copper in the Carpathian sea would lead to its syngenetic deposition with variegated shales (Monasterzec, Strzyżów, Męcina near Limanowa etc. — Gruszczuk & Ostrowicki 1961 a, b; Kita & Ostrowicki 1959; Kita & Badak 1959). On the other hand alkali polysulphide solutions were subjected to multistage chemical alterations. They consisted in hydrolysis, capture by pyrite and markasite forming within Flysch clays and decomposition into simple sulphides caused by the action of manganese oxides associated with radiolarites, spongiolites and sideritic concretions. Under these conditions polysulphides are oxidized according to the previously presented equations into realgar accompanied by trace amounts of orpiment, sphalerite and galena.

It is, however, interesting that the distribution of traces of copper in the Carpathian rocks is not similar to that of arsenic. The latter is present in pyrite concretions occurring in grey-greenish claystones overlying Cretaceous variegated shales. According to Michałek's data (1962) the As content in these pyrites increases when approaching the realgar deposit in Rabe:

Locality	Cu ppm	As ppm	Atomic ratios		
			Cu	As	Cu/As
Bezmiechowa near Monasterzec	85	90	1.33	1.20	1.10
Bystre near Baligród	165	170	2.59	2.26	1.14
Jablonka near Baligród	95	195	1.49	2.60	0.57
Rabe	105	260	1.65	3.47	0.47

Basing on the above data it is difficult to establish the chemical composition of solutions and what mineral of the primary deposits was leached. Moreover, because of lack of data on the volume ratio of copper-bearing shales (average Cu content 0.02 wt. per cent) and pyrite concretions (average As content 200 ppm) it is very difficult to establish the average Cu/As ratio in this environment. When assuming that the thickness of Cu- and As-enriched zone does not exceed 10 cm, the approximate Cu/As ratio would amount to 100:1. Such ratio is characteristic for tetrahedrites from Transylvanian deposits (Botes: 37% Cu and 0.38% As). While assuming the presence of polysulphides of tetrahedritic chemical composition, the antimony (antimonite) would be concentrated in deeper parts of Flysch series or even in the basement rocks.

Separate migration of copper and arsenic in the Carpathian basin and their different behavior during syngenetic processes accompanying the formation of Flysch deposits is comprehensible if we take into account easy solubility of copper compounds and its tendency to form diverse mineral phases. On the other hand slow migration of arsenic depends upon amphoteric character of this element and the susceptibility of solutions of its compounds to hydrolysis.

The localization of arsenic deposit under consideration in the environs of Baligród i.e. far from Transylvanian and Slovakian young-volcanic ore deposits is an important argument for connecting its origin exclusively with the basement underlying the Carpathian Flysch.

REFERENCES

- (BARISHNIKOV E.K., MERLIKH B.V., SLAVSKAYA A.I.) 1957: БАРИШНИКОВ Е.К., МЕРЛИХ Б.В., СЛАВСКАЯ А.И. — Метациннабарит из Закарпаття. — Минер. Сб. 11.
- GAWEŁ A., 1931: Granite aus den Krosnoschichten in der Umgebung von Sanok. — Bull. Acad. Polon. Sci. Let. ser. A.
- GAWEŁ A., 1932: Granophyre und Porphyre aus den Flyschkarpaten in der Umgebung von Sanok. Ibidem.
- (GRIGORYAN G.O.) 1960: ГРИГОРЬЯН Г.О. — О некоторых закономерностях и условиях образования свинцово-сурьмяных руд. — Геохимия.
- GRUSZCZYK H., OSTROWICKI B., 1961a: Mineralizacja miedzią fliszu karpackiego. — Pr. geol. Kom. Nauk. Miner. PAN Oddz. w Krakowie, 3.
- GRUSZCZYK H., OSTROWICKI B., 1961b: Występowanie miedzi w pstrych utworach fliszu karpackiego w Męcinie koło Limanowej. — Spraw. Pos. Kom. Nauk. Geol. Oddz. PAN Kraków.
- HEMPEL J., 1933: Sprawozdanie z badań wykonanych w r. 1932 nad złożami rudy manganowej w okolicach Sanoka, Krosna, Jasła i Gorlic. — PIG Pos. nauk. 36.

GENEZA REALGARU W UTWORACH FLISZOWYCH OKOLIC BALIGRODU (KARPATY FLISZOWE)

Streszczenie

Artykuł zajmuje się genezą realgaru występującego w szczelinach iłołupków i w zsylikowanych piaskowcach hieroglifowych wieku eoceńskiego. Autor przyjmuje istnienie roztworów wielosiarczków alkalicznych pochodzących z podłoża krystalicznego pod fliszem, sygnalizującego swą obecność pojawianiem się egzotycznych otoczków granitu, łupków mikowych i amfibolitów w oligoceńskich piaskowcach krośnieńskich. Roztwory wielosiarczków stanowiły bądź dalszy ciąg epimagmowych żył mineralnych w krystaliku podłoża, bądź powstały przez wymywanie tych żył przez solanki fliszowe. Przesiakiując przez utwory fliszowe uległy w strefie hipergenicnej częściowemu utlenieniu pod wpływem tlenków manganu, tworzących naskorupienia w szczelinach iłołupków i piaskowców oraz pseudomorfozy po manganowych sferosyderytach. Towarzyszące wielosiarczkom metale ciężkie zaznaczyły się obecnością śladów sfalerytu w złożu realgaru oraz rozproszaniem rud miedzi w pstrych iłach okolic Załuża i Monasterca. Świadczyć też o nich mogą ślady rtęci czy cynobru wspomniane w publikacjach z XVII i XVIII wieku (Jonston 1633, Rzączyński 1721).

Антони ГАВЕЛ

ГЕНЕЗИС РЕАЛЬГАРА ВО ФЛИШЕВЫХ ПОРОДАХ ОКРЕСТНОСТЕЙ С. БАЛИГРУД (ФЛИШЕВЫЕ КАРПАТЫ)

Резюме

Статья посвящена рассмотрению генезиса реальгара, распространенного в трещинах среди глинистых сланцев и окремельных иероглифовых песчаников эоценового возраста. Автор высказывает предположение о существовании растворов полисульфидов щелочных элементов связанных с кристаллическим подфлишевым основанием, породы которого — граниты, слюдяные сланцы и амфиболиты — представлены в гальке, перетолженной в кросненских песчаниках олигоценного возраста. Полисульфидные растворы являлись либо остатком после образования эпимагматических минеральных даек в кристаллическом основании, либо же возникли в результате выщелачивания этих жил флишевыми рассолами. Просачиваясь сквозь флишевые породы эти растворы в зоне гипергенеза подверглись частичному окислению под действием окислов марганца, образующего коркообразные налеты по трещинам в сланцах и песчани-

- JONSTON J., 1633: Thaumatrographia naturalis.
KAMIENSKI M., 1937: O minerałach arsenowych z fliszu karpackiego okolicy Leska. — Arch. miner. 12.
KITA M., BADAŁ J., 1959: Występowanie miedzi w Żyznowie koło Strzyżowa. — Prz. geol. 4.
KITA M., OSTROWICKI B., 1959: Mineralizacja miedzią w Monastercu koło Leska. — Kwart. geol. 3/4.
KREUTZ S., GAWEL A., 1926: Essai d'une caracteristique des roches dans le profil Boryslaw-Mrażnica-Schodnica. — Mem. I. Reun. Assoc. Carpat. Pologne. Serv. Geol. Pol. — St. Boryslaw.
KUŹNIAR C., 1932: Rudy manganowe w Trepczy i Glinicach pod Sanokiem. — PIG Pos. nauk. 35.
KUŹNIAR C., KRAJEWSKI R., 1933: Sprawozdanie z badań rud manganowych wykonanych w r. 1932. — PIG Pos. nauk. 36.
LILL VON LILIENBACH, 1830: Ein Durchschnitt aus den Alpen mit Hindeutung auf die Karpaten. — Jahrb. f. Min. Geogn. Geol. u. Petrefactenkunde.
(LAZARENKO E. K.), 1957: ЛАЗАРЕНКО Е. К. — Обший минералогический очерк Закарпаття. — Минер. Сборник 11.
MICHAŁEK Z., 1962: Studium geochemiczne siarczkowych minerałów żelaza. — Pr. geol. Kom. Nauk. Geol. PAN Oddz. w Krakowie, 6.
NAREBSKI W., 1957: Mineralogia i geochemiczne warunki genezy tzw. syderytów fliszu karpackiego. — Arch. miner. 21.
(NESTEROVA Y. S.), 1960: НЕСТЕРОВА Е. К. — О химических исследованиях блеклых руд. — Изв. АН СССР сер. геол. (1).
(PIOTROWSKI H.), 1958: ПИОТРОВСКИ Г. — К вопросу о генезисе киобари и метацинобарита. — Минер. Сб. 12.
(PIOTROWSKI H.), 1961: ПИОТРОВСКИ Г. — Соотношение киобари и метацинобарита в закарпатских месторождениях. — Материалы Ком. Мин. Геох. 4 Съезда Карпато-Балканск. Ассоциации.
RZĄCZYŃSKI G., 1721: Historia naturalis curiosa Regni Poloniae.
SAVUL M., ABABI V., BOTEZ C., MOVILEANU A., 1963: Contributions à la connaissance de la distribution des elements mineurs dans le profil geochimique des Carpates orientales. — Comm. V Congr. Assoc. Geol. Carp.-Balk. Bucuresti.
SAVUL M., BOTEZ C., JEANRENAUD P. J., JONES L., NACU A., 1963: Distribution des plusieurs elements rares (Cu, Pb, Zn, Co, Ni, Mn, P) dans les formations du flysch des Carpathes orientales (Roumanie). — Res. Comm. VI Congr. Assoc. Geol. Carp.-Balk. Varsovie.
SIEGEL A., 1951: Skala diabazowa jako egzotyk w kredowych utworach karpaczych. — Roczn. Pol. Tow. Geol. 20.
ŚLĄCZKA A., 1959: Stratygrafia serii śląskiej Łuski Bystrego na południe od Baligrodu. — IG Biul. 131.
ŚLĄCZKA A., 1961: Geneza poziomu egzotykowego z Bukowca koło przełęczy Użockiej. — Roczn. Pol. Tow. Geol. 31.
ŚLĄCZKA A., WIESER T., 1962: Łupki z egzotykami z warstw krośnieńskich w rejonie Baligrodu. — Kwart. geol. 4.
WOJCIECHOWSKI J., 1950: Złoto rodzime i minerały towarzyszące w żyłach kruszcowej pod Szczawnicą. — Acta geol. Pol. 1.
ZŁOTNICKA J., 1960: Korelacja horyzontów ropnych pola naftowego Tarnawa-Wielopole-Poraż na podstawie jakościowego składu pierwiastkowego popiołów rop metodą analizy spektrograficznej. — Pr. Inst. Naft. 64.

ках и псевдоморфозы по марганцевым сферосидеритам. Растворы щелочных полисульфидов сопровождались тяжелыми металлами, о чем свидетельствуют следы сфалерита в рудопроявлениях реальгара и меднорудные проявления в пестрых глинах района местностей Залуже и Монастеж. Кроме того, это подтверждается следами ртути и киновари, о которых упоминается в публикациях XVII и XVIII в.в. (Йонстон 1633, Жончиньски 1721).