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PRELIMINARY REPORT ON THE OCCURRENCE OF PALLADIUM MINERALS IN ZECHSTEIN ROCKS OF THE FORE-SUDETIC MONOCLINE

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Abstract. Geochemical and mineralogical data concerning the occurrence of palladium minerals in Zechstein rocks is discussed. It has been found that organic compounds of palladium have the primary character. Palladium minerals are secondary, owing their origin to decomposition of organic molecules with Pd and its redeposition as Pd-As and Pd-As-S compounds. Microprobe analyses have revealed the presence of a series of palladium compounds, viz.: Pd_5As_2 , PdAs_2 , Pd_3As_2 , Pd (Co, Ni, Ag)As, PdAs, $\text{Pd}_4\text{As}_2\text{S}$ and $\text{Pd}_4\text{As}_2\text{S}_2$. These minerals display optical features and chemical composition different from the natural palladium phases that have been known heretofore. It is the first recorded occurrence of palladium minerals connected with the diagenetic-sedimentary cycle.

After submitting this paper to the Editors, the article entitled: New data on some palladium arsenides and antimonides, written by L. J. Cabri, J. H. G. Laflamme, J. M. Stewart, J. F. Rowland and T. T. Chen has appeared in Canadian Mineralogist 1975 v. 13, pp. 321—335. It deals with palladium minerals similar to those discussed in this paper: Pd_6As_2 , Pd_5As_2 , Pd_2As , (Pd, Ni, As), (Pd, Cu, As).

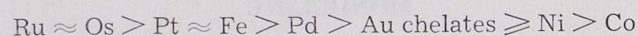
GEOCHEMISTRY OF PALLADIUM IN ZECHSTEIN ROCKS

The knowledge of behaviour of platinum metals in weathering zone and in sedimentary cycle is very unsatisfactory. The data on their content in sedimentary rocks are scanty and incomplete. Particularly interesting is the increase in the platinum metals content in bituminous shales and in coal ashes (Crocket 1969). These elements were found to behave in a similar way in the Zechstein rocks of the Fore-Sudetic monocline. It has been shown by semi-quantitative method of emission spectrography that in some fractions of organic compounds extracted from kerogen the content of Pd, Pt, Ru? amounts up to 10 ppm and that of Rh up to 5 ppm. The association of platinum metals with organic compounds is important

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because of the genesis of palladium minerals. None of the minerals of other platinum metals has been recorded there so far. The microprobe analyses have also shown a slight, if any, admixture of platinum metals in Pd minerals. The source of palladium for its new formed minerals is to be sought presumably in the organic compounds decomposed during diagenesis. Since Pd minerals are practically free from other platinum metals, organic compounds displaying low stability for palladium should be looked for. As the platinum content seems to be the second highest after palladium, organic compounds showing a greater stability for Pt than for Pd are practically involved. These could be the olefin complexes, which show the stability series $Pt > Pd > Ni$ (Coates *et al.* 1968). It is very probable since palladium minerals are fairly frequently associated with nickel (to lesser extent Co) and form sometimes and admixture in $NiAs_2$ amounting to 1.5 wt. %.

Judging from theoretical data and laboratory investigations (Coates 1956, Coates *et al.* 1968), the group of sandwich compounds — metallocenes seems to be more promising. The properties of metallocenes suggest that the stability series of these compounds under natural diagenetic conditions could be as follows:



This sequence of the stability series is well in accord with the results of geochemical investigations of palladium minerals since it accounts for:

- 1) the lack of other platinum metals in the structure of palladium minerals,
- 2) the occurrence of some Pd minerals in paragenesis with electrum and for the Au admixture in these minerals,
- 3) the lack of Fe in Pd minerals; if however, iron does appear, this fact is accompanied by an increase in the Pt content exceeding the detectability limit of the electron microprobe method,
- 4) the occurrence of Pd minerals in paragenesis with nickel diarsenides, and also for a Pd admixture in $NiAs_2$ amounting occasionally to 1.5 wt. %.

It should be added here that palladium minerals have been found so far in secondary concentrations, frequently in paragenesis with electrum. This fact indicates that the genesis of palladium mineralization is similar to that of gold (Kucha 1974), i.e. during diagenesis organic palladium compounds were decomposed and redeposited as secondary concentrations in the rocks directly underlying the shales.

The presence of organic compounds of platinum metals in the Zechstein bituminous shales is unquestionable. The interpretation, on the other hand, that these complexes are sandwich compounds (metallocenes) is but a hypothesis.

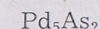
Electron microprobe analyses of the content of platinum metals in the minerals have shown that the content of these elements in native gold, native silver and native bismuth is below the detectability limit of the microprobe method. The most meaningful connection has been found to exist between palladium and nickel diarsenides.

PALLADIUM MINERALS IN ZECHSTEIN ROCKS

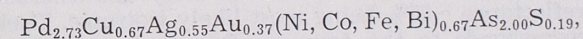
The microprobe analyses have revealed the presence of a series of palladium minerals. They are arsenides containing sometimes a substantial amount of sulphur. The main cations that accompany palladium in its minerals are: Ag, Cu, Ni, Au, Bi. The analyses have failed to show the presence of Sb, Te, Ge, Se or Sn.

ORGANIC PALLADIUM COMPOUNDS

The microprobe analyses have shown the presence of small concentrations of organic Pd compounds. They are about 10 μm in size, sometimes have geometrically regular shapes, and their reflectance is ca 10%. The palladium content in such concentrations amounts to 2 wt. %, being higher than that of other platinum metals. It is interesting to note that Au is missing in the compounds of that type, and that the content of Bi and Pt is similar to Pd while that of S is somewhat lower.



A mineral of this composition has not yet been recorded. Most approximate in composition is arsenopalladinite $Pd_5(As, Sb)_2$ containing > 5 wt. % of Sb (Clark *et al.* 1974). In the Zechstein rocks, a mineral with the optical properties similar to those of arsenopalladinite has been found. It occurs in paragenesis with electrum, occasionally acting as a contact zone between gold and other palladium minerals. Its grain size is small, hence no optical properties except $R = 52\%$ could be determined. The composition of this mineral corresponds to the formula:



so it differs from arsenopalladinite (Clark *et al.* 1974). It is interesting to note the high Au content, amounting sometimes up to 20–25 wt. %. It may be, therefore, both an Au and Pd arsenide. Though such gold compounds have not been recorded so far, laboratory investigations suggest a possibility of occurrence of compounds of the As-Au type (Hansen, Anderko 1958). It could be then a new mineral, since its chemical composition differs considerably from that of arsenopalladinite.

In the group of solid phases similar to Pd_5As_2 , the presence of a compound of the $Pd_{3.21}Ag_{0.60}Cu_{0.49}Ni_{0.22}(Au, Co, Bi, Fe)_{0.09}As_{2.00}S_{0.17}$ type has been found. It is brown-grey, anisotropic, its reflectance is 18%, and it shows weak bireflectance in air. Considering its chemical composition and optical features it seems to be a new mineral.



No mineral of this composition has been recorded yet. Its reflectance in air is 60%, it is white and weakly anisotropic. It is paragenetic with the cobaltite-gersdorffite series. The mean chemical composition of this phase corresponds to $Pd_{0.87}Ag_{0.06}(Ni, Co)_{0.05}(Cu, Au)_{0.01}As_{2.00}$. It is one of the purest palladium phases recorded in the Zechstein deposits. The only essential admixture, though occurring in small amount, is silver.

Pd₃As₂

The mineral approximating in composition to Pd₃As₂ is of brassy-brown colour, with R ca 30%. Most probably it is isotropic; considering however, small grain size, this is by no means certain. It is associated with dolomite and native gold. Its chemical composition corresponds to the formula: Pd_{2.53}Ag_{0.48}Cu_{0.13}(Ni, Co, Au)_{0.15}As_{2.00}S_{0.28}.

Pd(Co,Ni,Ag)As

An inclusion of a palladium mineral with a slightly higher reflectance and showing white colour has been found in nickel cobaltite Co_{0.65}Ni_{0.35}AsS. It has a high content of Co, Ni and Ag. The chemical composition of this mineral corresponds to the formula: Pd_{0.99}Co_{0.45}Ni_{0.28}Ag_{0.16}Cu_{0.03}As_{1.00}S_{0.12}.

PdAs

One of the microprobe analyses has revealed the presence of fine grains of a mineral showing composition corresponding to Pd_{1.06}Ni_{0.11}As_{1.00}S_{0.14}. Considering the small size of the mineral in question, its optical properties are not well defined.

PALLADIUM SULPHIDE-ARSENIDES (Pd₄As₂S-Pd₄As₂S₂)

When performing the microprobe analyses, two varieties of compounds of the Pd-As-S type have been detected. They are characterized by a rather low reflectance ~35%, being most likely isotropic. Their chemical composition corresponds to the formula: Pd_{3.91}Cu_{0.37}Ag_{0.35}(Au, Fe, Ni, Te, Hg)_{0.21}As_{2.00}S_{0.98} and Pd_{3.62}Cu_{0.44}Ag_{0.16}(Fe, Ni, Hg, Bi, Co)_{0.68}As_{2.00}S_{2.24}.

Comparing chemical composition and optical properties of the discussed minerals with the known palladium phases, practically all of them could be regarded as being new. A question then arises if such an interpretation is correct. The following fact may be adduced in its support: during investigations of synthetic palladium arsenides, seven distinctly different phases of the composition between PdAs₂ and Pd₅As have been distinguished (Saini *et al.*, vide Clark *et al.* 1974). Moreover, for the majority of palladium compounds discovered in the Zechstein deposits, may be found equivalent compounds formed by other elements of the group VIII of the periodic system. Further confirmation results from a close association between Ni and Pd in the discussed palladium minerals and between Pd and Ni in Ni and Ni-Co minerals. If, additionally, we take into account high Ag content determining in some cases the character of compounds formed, such a great number of new solid phases is quite possible. This is the first report on Pd minerals associated with sedimentary rocks. They are formed under completely different conditions than the platinum group minerals known so far. The decomposition of organic palladium compounds and redeposition of this metal proceeded at low temperatures, which suggest the possibility of occurrence of a number of additional, temperature-unstable phases.

CONCLUSIONS

1. The occurrence of organic compounds of platinum metals (mainly Pd and Pt) have been recorded in the Zechstein rocks.
2. Palladium minerals are encountered in rocks directly underlaying the bituminous shale as secondary mineral concentrations.
3. Palladium minerals in question originated presumably during diagenesis. Organic Pd compounds from black shales were decomposed and the metal was redeposited as arsenides and sulphide-arsenides.
4. Specific conditions of this mineral-forming process (essentially low temperature and the presence of organic compounds) gave rise to a series of new palladium minerals that have not been recorded yet.

A more detailed discussion of the presented problem will be soon published.

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WYNIKI WSTĘPNE BADAŃ NAD WYSTĘPOWANIEM MINERAŁÓW PALLADU W SKALACH CECHSZTYŃSKICH MONOKLINY PRZEDSUDECKIEJ

Streszczenie

Przedyskutowano dane geochemiczne i mineralogiczne dotyczące występowania minerałów palladu w skałach cechsztyńskich. Stwierdzono, że występujące w nich organiczne związki palladu mają charakter pierwotny. Siarczkowe i arsenkowe minerały palladu są wtórne i zawdzięczają swe powstanie rozkładowi organicznych połączeń Pd, a następnie ich redepozycji jako związki typu Pd-As i Pd-As-S. W wyniku badań za pomocą mikroskopy elektronowej stwierdzono serię związków palladu: Pd₅As₂, PdAs₂, Pd₃As₂, Pd(Co, Ni, Ag)As, PdAs, Pd₄As₂S oraz Pd₄As₂S₂. Wykazują one cechy optyczne i skład chemiczny odmienny od znanych dotychczas minerałów Pd. Jest to pierwsze znane występowanie minerałów Pd związane z cyklem diagenetyczno-sedymentacyjnym.

**ДАнные ПРЕДВАРИТЕЛЬНЫХ ИССЛЕДОВАНИЙ МИНЕРАЛОВ
ПАЛЛАДИЯ, ПРЕДСТАВЛЕННЫХ В ЦЕХШТЕЙНОВЫХ ПОРОДАХ
ПРЕДСУДЕТСКОЙ МОНОКЛИНАЛИ**

Резюме

Описаны геохимические и минералогические условия распространения минералов палладия в породах цехштейна. Констатируется, что наблюдаемые в этих породах органические соединения палладия имеют первичный характер. Сульфидные и арсенидные минералы палладия представляют вторичные соединения, образовавшиеся за счет распада органических соединений и последующего переотложения в виде соединений типа Pd-As и Pd-As-S . С помощью электронного микрозондирования был определен ряд соединений палладия: Pd_5As_2 , PdAs_2 , Pd_3As_2 , $\text{Pd}(\text{Co}, \text{Ni}, \text{Ag})\text{As}$, PdAs , $\text{Pd}_4\text{As}_2\text{S}$ и $\text{Pd}_4\text{As}_2\text{S}_2$. Они характеризуются другими оптическими свойствами и химическим составом по сравнению с ранее известными минералами палладия. Описанное местонахождение минералов палладия является первым проявлением, наблюдавшимся в условиях связи с седиментационно-диагенетическим циклом.