Zbigniew SAWŁOWICZ*

SIGNIFICANCE OF METALLOPORPHYRINS FOR THE METAL ACCUMULATION IN THE COPPER-BEARING SHALES FROM THE ZECHSTEIN COPPER DEPOSITS (POLAND)

Abstract. The vanadyl and nickel porphyrins were found in the resin fraction of bitumen extracted from high organic copper-bearing shale of the Zechstein copper deposits (Poland). Apart from the more common types of porphyrins (Etio and DPEP) the presence of rhodoporhyrins is also suggested. No significant relation between the content or type of metalloporphyrins in resins and chemical composition of mineral and organic matter of shale was found. It is suggested that the major part of vanadium could be present in shale as vanadyl porphyrins. There are no metallo-porphyrins in resins from oxidized copper-bearing shale. The significance of metalloporphyrins in processes of copper and other metals accumulation in copper-bearing shale is considered.

INTRODUCTION

The relation between metals and organic matter in the copper deposits of the Fore-Sudetic monocline has been suggested for a long time. It is based on positive correlation between organic carbon and some heavy metals occurring in these deposits, e.g. Cu, Ag, V, Mo, Mn and Ni (Harańczyk 1972, Tokarska 1971, Wojcie-chowska, Wojciechowski 1979, Kucha, Sawłowicz 1980 and others). However, there are still very scarce information on the form and the character of coexistence of metals and organic matter.

Tokarska (1971) noticed the vanadyl porphyrins in some resins from the Fore--Sudetic copper-bearing shales. This fact stimulated the present author to investigate in this aspects several samples of high organic copper-bearing shales characterized also by mineralogical-geochemical studies. Resins from the copper bearing shale bitumen were studied in this work. Shale samples were collected from all parts of mines of the Lubin—Sieroszowice area. The majority of shale samples include high-organic shales with highest copper content, other few samples are dolomitic shales. Some shale samples are hardly mineralized and their organic matter show some weathering features.

*Jagellonian University, Institute of Geological Sciences, Cracow (Kraków, ul. Oleandry 2a).

3*

METHODS

After crushing and milling the shale samples were subjected to extraction by chloroform for 24 hours in a Soxhlet apparatus. The resulting extracts were divided into four basic groups of bitumen on a silica-alumina chromatographic column. Resins were eluted by benzen-metanol mixture (1:1). Resins spectra in the near-violet and visible range were recorded on UV-VIS spectrophotometer M 40 (C. Zeiss Jena). The spectra were taken shortly (1—2 hours) after the solution of resins in chloroform. A short contact of porphyrins with chloroform is not dangerous (Howe 1961). In addition, a few spectra of the same solutions were recorded after six days.

RESULTS

Most of the spectra of the studied resins show absorption bands typical of metalloporphyrins: about 400 nm (Soret band) and in 500—600 nm region (Fig. 1). Spectra of all samples showing rich ore mineralization display absorption bands related to the vanadyl porphyrins (VO-porphyrins): 407 nm (Soret) and 572 nm (α). In the spectra with more intensive 572 nm band the weak absorption band at 532 nm (β) is also observed. The majority of samples show the absorption bands related to the nickel porphyrins (Ni porphyrins): 391 nm (Soret) and about 550 nm (α) (the later is the most intensive absorption band for these porphyrins in the visible region).

In the spectra of resins showing higher metalloporphyrins content the minor absorption band at about 595 nm is also present. It is thought to be related to rhodo type porphyrins (Baker 1969, Millson et al. 1966). No absorption bands of metalloporphyrins in resins extracted from the clay-organic shales without mineralization were observed.

The intensities of the absorption bands of Ni- and VO-porphyrins highly vary among spectra. No significant correlation between the type or content of metalloporphyrins and the chemical composition of organic matter and mineralogical-geochemical composition of shales was found.

In comparison with the spectra of chloroform solutions prepared shortly before recording, those recorded after six days do not show any absorption bands related to Ni-porphyrins.
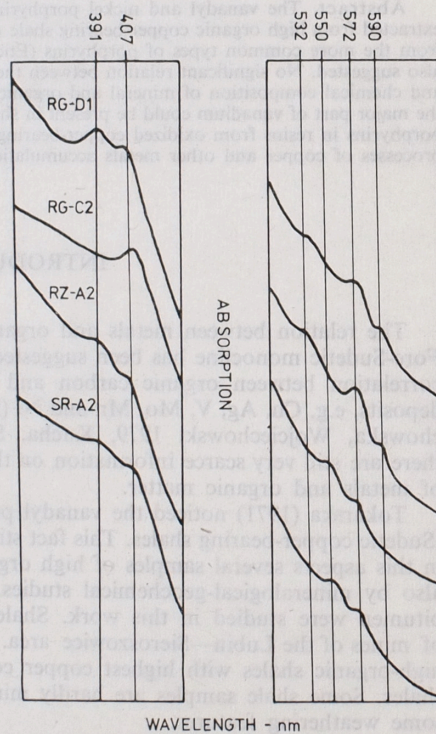

Fig. 1. Electronic spectra of the nickel and vanadyl porphyrin mixtures with different portion of each compound

DISCUSSION

Porphyrins are widely distributed in sediments and sedimentary rocks, especially those which were not extensively oxidized. In most cases porphyrins are the members of both etio and DPEP series where the later predominates (Hodgson, Whiteley 1980). In some cases the third type — rhodo, is also present. Porphyrins exist in rocks mainly as metalloporhyrins which are relatively stable. The complexing metals are mainly V (vanadyl) and Ni, very rare Fe and Cu.

The domination of etio type over DPEP type porphyrins in studied samples is possible. The ratio of DPEP to etio components decrease with increasing time of burial of a sediment (Mackenzie et al. 1981).

The presence of rhodoporphyrins in the samples studied is probably due to their secondary origin as a result of Eh-pH oscillations related to diagenetic and mineralizing processes. It is possible that rhodo type porphyrins originate from more common porphyrins during oxidizing phases in their history (Millson et al. 1966).

The lack of metalloporphyrins in the resins from the shales without mineralization can be the result of oxidizing processes, both primary and/or secondary. On the one hand porphyrins originate and are stable only in anaerobic environments (Lewan, Maynard 1982). On the other hand, degradation of porphyrin complexes can be due to processes of oxidizing of bitumen, for example, during a contact with oxygenated groung waters (Hodgson et al. 1967, Dean, Whitehead 1963). Oxidizing processes must persist long time and/or to be intensive because degradation of porphyrins is slow (Costantinides, Arich 1962). It is possible that the des troying of chlorins (which are precursors of porphyrins) by microflora (Swain et al. 1964, vide Hodgson 1973) connected with oxidation processes during the early stages of diagenesis resulted in the lack of metalloporphyrins in some shales.

The domination of vanadyl ovar nickel porphyrins in the samples studied is understandable in regards of their stronger tendency to concentrate in marine strata and their higher stability in more severe temperature and acidic conditions (Hodgson et al. 1967, 1968).

The lack of correlation between rock characteristics (chemical and petrographical composition of organic matter) and porphyrin types and their content confirm earlier observations (Hodgson et al. 1967, 1968, Lewan, Maynard 1982, Spiro et al. 1983). The relation between the VO- and Ni-porphyrins and the sulphur content in bitumens suggested earlier by Radczenko and Sesina (1955) was not confirmed in this study.

Apart from the bitumen (up to one wt. percent), the dominating form of organic matter in the high organic copper-bearing shale from the Fore-Sudetic monocline is kerogen. Its content is up to 20 wt. percents of the whole rock (Sawłowicz, in press). Thus, the evidenced presence of metalloporphyrins in studied bitumen is important, especially when one considers a possible presence of metalloporphyrins in kerogen, built in its cross-linked, polymeric structure (Blumer, Snyder 1967). In their recent study, Spiro and coworkers (1983) found the relation between Ni and V complexation of tetrapyrroles pigments in bitumen and in kerogen. If it were confirmed it would be of great importance in consideration upon geochemistry of nickel and vanadium, or even other metals, in copper-bearing shale. It would be interesting especially in the case of vanadium, the own minerals of which have not been found yet in the Fore-Sudetic copper-bearing shale. The V and Ni contents in the copper-bearing shale from the Fore-Sudetic monocline are 900—1000 ppm (Wojciechowska, Serkies 1969, Kucha, Sawłowicz 1980) and about 300 ppm (Kucha, Sawłowicz 1980), respectively.

According to Lewan and Maynard (1982), V and Ni concentrations as tetrapyrroles complexes in bitumen from different rocks vary between 0.2—4760 ppm V and 7—1240 ppm Ni. Kerogen consists of 10—20 percent of a whole copper-bearing shale and there is a possibility of even higher Ni- and VO-porphyrins concentrations in kerogen than in bitumen, mainly due to much higher nitrogen content in kerogen in comparison with bitumen (three and one percent, respectively). Thus, we may assume that almost all nickel and vanadium can be bound to porphyrin complexes, mostly during accumulation of clay-organic sediment and its diagenesis. Probably, most of the vanadium has been complexed by porphyrins so far. Nickel, since its porphyrin complexes are more sensitive to diagenesis, is actually present in the copper-bearing shale mostly in sulfide minerals and only subordinately in the porphyrin complexes.

The concentration of the VO- and Ni-porphyrins in the copper-bearing shale allows to consider a possibility of existence of copper porphyrins in this shale and their role in the copper concentration processes. Copper porphyrin complexes are formed easier than those of Ni or V and they could be an intermediate in their formation (Hodgson 1960). In this context, it is valuable to stress the possitive correlation between copper and vanadium in the Fore-Sudetic copper-bearing shale (Wojciechowska, Serkies 1969). Incorporation of copper ion into free porphyrins is especially facile (Hambright 1975, vide Bergaya, Van Damme 1982). Cu-porphyrins are also quite stable in a homogenous medium (without clay minerals, for example (Buchler 1975, Hambright 1975 vide Bergaya, Van Damme 1982). Lewan and Maynard (1982) suggest that Ni and V are concentrated in bitumen as the tetrapyrrole complexes mainly due to their availability in anaerobic system, small ionic radii and favourable electron configuration. One can consider whether these requirements are fulfilled in the case of copper.

It seems that during the sedimentation of the copper-bearing shale and its early diagenesis, anaerobic conditions prevailed and sea water of abnormal composition (high content of copper and other metals) (Wedepohl 1964, 1980, Harańczyk 1972) was a huge and easy available source of copper.

Bivalent copper cation shows the most similar ionic radius (from all other cations of the first transition series) to Ni and VO. The same refers to ligand stabilization energy in the octahedral and square planar configuration (vide Lewan, Maynard 1982).

High amount of tetrapyrrole complexes is needed for enrichment of a sediment in metals. Organic matter derived from algae is an excellent source of porphyrins. Phytoplankton can contain up to 67.000 ppm of chlorophyl (vide Lewan, Maynard 1982), the main precursor of tetrapyrroles. Apart from algae, the minor source of organic matter in a copper-bearing shale could be sulphate-reducing bacteria of Desulphovibrio sp. which are also suppliers of porphyrins (Hodgson, Whiteley 1980). Thus, it is reasonable to assume that the favourable conditions for forming copper porphyrin complexes existed during the copper-bearing shale sedimentation.

The complexation of copper by porphyrins in kerogen is highly probable since the EPR studies of humic acids (Nissenbaum at al. vide, Nissenbaum, Swaine 1976, Goodman, Cheshire 1973, Cheshire et al. 1977) showed that copper is complexed in humic acids by the azote of porphyrins. Humic acids are thought to be precursors and/or part of young kerogens (Ishiwatari 1979).

Copper complexation by porphyrins could take place during the accumulation and the earliest phases of diagenesis of clay-organic sediment, before its lithification. The source of copper could be interstitial waters and clay minerals as well. In the case of interstitial waters the most important factors would be: 1) copper concentration in water, 2) the amount of free porphyrin complexes, 3) the rate of metal diffusion from the overlying water body to a sediment, 4) the period of opening of water-sediment system. As high as 39 ppb of dissolved copper was recorded in the interstitial waters of marine sediments (Presley et al. 1967, 1972). Clay minerals are not only carriers transporting metals on their surfaces (Caroll 1958) but also can be a source of metal ions for metalloporphyrin formation (Cady, Pinnavaia 1978, Bergaya, Van Damme 1982). Cady and Pinnavaia (1978) have shown that during the contact of free base porphyrins with the Cu-montmorillonites the copper porphyrins form on their surfaces and then are relieved to solution in metallized form. However, Bergaya and Van Damme studies (1982) proved a low stability of Cu-porphyrins in presence of clay minerals what could explain their rarity in natural environments (Palmer, Baker 1978, Galimov et al. 1982). In comparison with Cu-porphyrins, the VO- and Ni-porphyrins have a great chance to survive the contact with clay minerals (Bergaya, Van Damme 1982). According to Bergaya and Van Damme (1982) the extensive formation of Cu-porphyrins from free base porphyrins in contact with Cu-montmorillonite and observed their low stability in contact with montmorillonite are not contradictory features but only show that the formation and demetallization rate constants are large and that the equilibrium constant is close to unity. In such a case, probably even small changes in oxidizing-reducing potential, the acidity and/or ion concentration during the early phases of accumulation and diagenesis of shale would render the predominance of one process over the other. However, we should keep in mind that the general tendency during the diagenesis is still the demetallization of Cu-porphyrins.

Most of the transition metals of the first series (Cu, Mn, Fe, Zn, Co, V and Ni) can form, in laboratory, metallic complexes with porphyrins. Because of different facility to form metalloporphyrin complexes and their different stability those metals could be selectively incorporated into porphyrin complexes. Relativele considerable facility of copper bonding to porphyrin complexes can result, to somy extent, in higher rate of copper ions diffusion from overlying water body to a sediment and thus in copper enrichment especially in an algal shale bed. Different stability of metalloporphyrin complexes can also be the cause of strong differentiation in the rate and time of metal sulfide precipitation during diagenesis.

It should be stressed that the porphyrins, although the best known, are only a part of highly complicated organic substances system, resulted in degradation of algal matter, which can also complexe a number of metals. However, this problem is beyond the scope of this paper and will be discussed later.

REFERENCES

BAKER E. W., 1969: Porphyrins. In G. Eglinton and M. T. J. Murphy (Editors): Organic Geochemistry, 464—497, Longman, Springer-Verlag, Berlin.
BAKER E. W., 1971: Porphyrins in deep ocean sources. Petroporphyrins from Challenger Knoll oil bearing cores. Chem. Geol. 7, 45—49.
BERGAYA F., VAN DAMME H., 1982: Stability of metalloporphyrins adsorbed on clays: a comparative study. Geoch. Cosmoch. Acta, 46, 349—360.
BLUMER M., SNYDER W. D., 1967: Porphyrins of high molecular weight in a Triassic oil shale: evidence by gel permeation chromatography. Chem. Geol., 2, 35—45.
CADY S. S., PINNAVAIA T. J., 1978: Porphyrin intercalation in mica-type silicates. Inorg. Chem. 17, 1501—1507.
CARROL D., 1958: Role of clay minerals in the transportation of iron. Geoch. Cosmoch. Acta 14, 1—27.

CHESHIRE M. V., BERROW M. L., GOODMAN B. A., MUNDIE C. M., 1977: Metal distribution and nature of some Cu, Mn, and V complexes in humic and fulvic acid fractions of soil organic matter. *Geoch. Cosmoch. Acta* 41, 1131—1138.

COSTANTINIDES G., ARICH G., 1963: Research on metal complexes in petroleum residues. Sixth World Petrol. Congres, Sect. 5, Paper 5, Paper 1.

DEAN R. A., WHITEHEAD E. V., 1963: The composition of high boiling petroleum distillates and residues. Sixth World Petrol. Congress, Sect. 5, Paper 9, Frankfurt.

GALIMOV E. M., KODINA L. A., BOGACHEVA M. P., SHIRINSKY V. G., 1982: Organic geochemical studies of samples from deep sea drilling project, Leg 64, Gulf of California. In: Init. Repts. DSDP, 64, 819—836, Washington.

GOODMAN B. A., CHESHIRE M. V., 1973: Electron paramagnetic resonance evidence that copper is complexed in humic acid by the nitrogen of porphyrin groups. *Nature* (Lond.), 244, 158—159.

HARAŃCZYK Cz., 1972: Mineralizacja kruszcowa dolnocechsztyńskich osadów euksynicznych Monokliny Przedsudeckiej. *Arch. Min.* 30. 13—173.

HODGSON G. W., 1973: Geochemistry of porphyrins-reactions during diagenesis. *Ann. New York Acad. Sc.* 206, 670—684.

HODGSON G. W., WHITELEY C. G., 1980: The universe of porphyrins. In: P. A. Trudinger, M. R. Walter, B. J. Ralph (Editors): Biogeochemistry of Ancient and Modern Environments, 35—46, Springer-Verlag.

HODGSON G. W., BAKER B. L., PEAKE E., 1967: Geochemistry of porphyrins. In: B. Nagy, U. Colombo (Editors): Fundamental aspects of petroleum geochemistry, 177—260, Elsevier.

HODGSON G. W., HITCHON B., TAGUCHI K., BAKER B. L., PEAKE E., 1968: Geochemistry of porphyrins, chlorins and polycyclic aromatics in soils, sediments and sedimentary rocks. *Geoch. Cosmoch. Acta* 32, 737—772.

HOWE W. W., 1961: Improved chromatographic analysis of petroleum porphyrin aggregates and quantitative measurement by integral absorption. *Anal. Chem.* 33, 255—260.

ISHIWATARI R., 1979: Insoluble organic matter in sediments and its geochemical role. In: Recent progress of natural sciences in Japan, 4, 103—110. Science Council of Japan.

KUCHA H., SAWŁOWICZ Z., 1980: Charakterystyka geochemiczna i mineralogiczna pierwiastków towarzyszących miedzi na obszarze kopalni Lubin Zachodni. *Geologia* (AGH), 6, 3, 53—70.

LEWAN M. D., MAYNARD J. B., 1982: Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geoch. Cosmoch. Acta* 46, 2547—2560.

MACKENZIE A. S., PATIENCE R. L., MAXWELL J. R., 1981: Molecular changes and the maturation of sedimentary organic matter. In: G. Atkinson and J. J. Zuckerman (Editors): Origin and chemistry of petroleum, 1—32, Pergamon.

MILLSON M. F., MONTGOMERY D. S., BROWN S. R., 1966: An investigation of the vanadyl porphyrin complexes of the Athabasca oil sands. *Geoch. Cosmoch. Acta* 30, 207—221.

NISSENBAUM A., SWAINE D. J., 1976: Organic matter-metal interactions in Recent sediments: the role of humic substances. *Geoch. Cosmoch. Acta* 40, 809—816.

PALMER S. E., BAKER E. W., 1978: Copper porphyrins in deep-sea sediments: a possible indicator of oxidized terrestrial organic matter. *Science* 201, 49—51.

PRESLEY B. J., BROOKS R. R., KAPLAN I. R., 1967: Manganese and related elements in the interstitial waters of marine sediments. *Science* 158, 906—910.

PRESLEY B. J., KOLODNY Y., NISSENBAUM A., KAPLAN I. R., 1972: Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia. II: Trace element distribution in interstitial water and sediment. *Geoch. Cosmoch. Acta* 36, 1073—1090.

[RADCZENKO O. A., SIESZYNA L. S.] РАДЧЕНКО О. А, СЕШИНА Л. С., 1955: О генезисе порфиридов в нефтях. *Докл. АН СССР* 106, 6, 1285—1288.

SAWŁOWICZ Z.: 1984: Badania substancji organicznej z łupków miedzionośnych z monokliny przedsudeckiej. *Przegl. Geol.* 7, 383—386.

SPIRO B., DINUR D., AIZENSHTAT Z., 1983: Evaluation of source, environments of deposition and diagenesis of some Israeli "oil shales" — n-alkanes, fatty acids, tetrapyrroles and kerogen. *Chem. Geol.* 39, 189—214.

TOKARSKA K., 1971: Geochemiczna charakterystyka substancji bitumicznej cechsztyńskich łupków miedzionośnych. *Kwart. Geol.* 15, 67—76.

WOJCIECHOWSKA J., SERKIES J., 1969: The occurrence of vanadium in the Fore-Sudetic Copper Deposits, Region of Lubin. *Bull. Acad. Pol. Sci.*, 17, 149—153.

WOJCIECHOWSKA R., WOJCIECHOWSKI W., 1979: Investigation of organic substance from the Fore-Sudetic Copper Deposit by the EPR method. *Bull. Acad. Pol. Sci.*, 27, 119—128.

WEDEPOHL K. H., 1964: Untersuchungen am Kupferschiefer in Nordwestdeutschland: Ein Beitrag zur Deutung der Genese bituminöser Sedimente. *Geoch. Cosmoch. Acta*, 28, 305—364.

WEDEPOHL K. H., 1980: The geochemistry of the Kupferschiefer Bed in Central Europe. In: S. Janković and R. H. Sillitoe (Editors): European Copper Deposits, 129—135, Belgrade.

Zbigniew SAWŁOWICZ

ZNACZENIE METALOPORFIRYN W PROCESIE AKUMULACJI METALI W ŁUPKACH MIEDZIONOŚNYCH Z CECHSZTYŃSKICH ZŁÓŻ MIEDZI (POLSKA)

Streszczenie

Frakcję żywic z bituminów wyekstrahowanych z ilasto-organicznego łupku miedzionośnego, tzw. smolistego, z monokliny przedsudeckiej poddano badaniom spektroskopowym w zakresie światła widzialnego i ultrafioletu. W żywicach (18 próbek) stwierdzono obecność porfiryn wanadylowych i niklowych (porfiryny typu etio i/lub DPEP). Obecne są prawdopodobnie również, w niewielkich ilościach, rodoporfiryny. Rodzaj metaloporfiryn i ich zawartość porównano ze składem chemicznym substancji organicznej oraz składem mineralogiczno-geochemicznym łupku, nie stwierdzając związku pomiędzy powyższymi parametrami.

Porównanie ilości bituminów i kerogenu w łupku oraz możliwość występowania porfiryn w kerogenie, skłania autora do przypuszczenia, że większość wanadu w łupku miedzionośnym może występować w formie przede wszystkim kompleksów porfirynowych.

Rozważono znaczenie udziału porfiryn w procesach koncentrowania miedzi i innych pierwiastków przejściowych w łupku. Autor sugeruje możliwość istnienia w czasie sedymentacji i wczesnych etapów diagenezy łupku miedzionośnego warunków sprzyjających tworzeniu się miedziowych kompleksów porfirynowych, które mogły w sposób znaczący selektywnie koncentrować miedź w łupku.

Nie stwierdzono obecności metaloporfiryn w żywicach pochodzących z łupku utlenionego, z bardzo ubogą mineralizacją kruszcową.

OBJAŚNIENIE FIGURY

Fig. 1. Widma absorpcyjne UV-VIS mieszanin porfiryn niklowych i wanadylowych z różnym udziałem poszczególnych składników

Збигнев САВЛОВИЧ

О ЗНАЧЕНИИ МЕТАЛЛОПОРФИРИНОВ В ПРОЦЕССЕ АККУМУЛЯЦИИ МЕТАЛЛОВ В МЕДИСТЫХ СЛАНЦАХ ИЗ ЦЕХШТЕЙНОВЫХ МЕДНЫХ МЕСТОРОЖДЕНИЙ (ПОЛЬША)

Резюме

Проводились спектроскопические исследования в диапазоне видимого света и ультрафиолета фракции смол из битумов, экстрагированных из глинисто-органогенного, так называемого смоляного сланца с Предсудетской моноклинали. В смолах (18 образцов) обнаружено присутствие ванадиловых и никелевых порфиринов (типа этио и/или DPEP). Вероятно, в небольших

количествах присутствуют также родопорфирины. Род металлопорфиринов и их содержание сопоставлялись с химическим составом органического вещества, а также с минералого-геохимическим составом сланца, причем связь между вышеупомянутыми параметрами не была обнаружена.

Сопоставление количества битумов и керогена в сланце, а также возможность присутствия порфиринов в керогене, склоняет автора предположить, что большинство ванадия в медистом сланце может присутствовать прежде всего в виде порфириновых комплексов.

Рассматривалось значение участия порфиринов в процессах концентрации в сланце меди и других переходных металлов. Автор предполагает возможность существования во время осадконакопления и ранних этапов диагенеза условий, содействующих образованию медных порфириновых комплексов, которые существенным образом могли селективно концентрировать медь в сланце.

Не обнаружено наличия металлопорфиринов в смолах, происходящих из окисленного сланца с весьма бедным оруденением.

ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. Спектры поглощения UV-VIS смесей ванадиловых и никелевых порфиринов с разным содержанием отдельных компонентов