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FRANCOLITE FROM THE LOWER ZECHSTEIN SEDIMENTS, RUDNA MINE, FORE-SUDETIC MONOCLINE

Abstract. Fluor-apatite (francolite) was found in lowermost part of Zechsteinkalk sequence i.e. in dolomitic shale, argillaceous dolomite occasionally in the top part of the Weissliegendes sandstone. Fluor-apatite content increases in the zinc-bearing shales. Francolite usually replaces fossil remnants e.g. algae, brachiopods etc. These textures suggest biogenic origin of francolite formed from P released from organic compounds during autooxidation of the organic matter.

INTRODUCTION

Lower Zechstein sediments are usually analysed for major and trace metals which are of economic interest. On the contrary, much less is known about the abundances of other trace elements e.g., phosphorus.

The occurrence of higher amounts of phosphorus and its minerals has been noted by some authors. Kucha (1976) mentioned apatite group minerals as one of accessories in copper-bearing shale. The same author (Kucha 1982) has described modifications of Lower Zechstein shale enriched in $\text{FeCa}(\text{PO}_4)$ — a new phase. This phosphate is intimately connected with the paragenesis of Au, platinum-group elements, mooihoeckite, haycockite and clausthalite. Mayer and Piestrzyński (1982) identified francolite in copper bearing shales from Rudna mine.

DISTRIBUTION OF PHOSPHORUS IN THE METAL-BEARING HORIZON

In Rudna mine the content of phosphorus in the Lower Zechstein metal-bearing shale amounts up to 0.033 wt% (arithmetic mean from 80 analyses). This value corresponds to lower limits of P contents in various modifications of Lower Zechstein shale presented by Kucha (1982). It also appears to be typical of copper-bearing shale which is the prevailing modification in Rudna area. In the Lower Zechstein dolomite the average content of P was found to be 0.027 wt.% (arithmetic mean from

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90 analyses) and in the white sandstone (Weissligendes) — 0.017 wt% (arithmetic mean from 79 analyses).

No distinct regularities have been observed in horizontal distribution of phosphorus in the investigated area excluding the obvious depletion in its content in the elevation zone of the Zechstein sea-floor which is connected with the decrease in thickness of the shale (Mayer, Piestrzyński 1985).

METHODS OF INVESTIGATION

X-ray diffraction studies was performed by means of TUR-M61A diffractometer using CoK_α radiation and powder technique.

Infrared absorption spectra were obtained with a Carl Zeiss UR-10 spectrometer, using KBr discs technique. Absorption spectra have been recorded in the range of wave numbers 100—1800 and 2800—3800 cm^{-1} .

The routine microscopic examinations of polished sections has led to identification of phosphate mineral. Its microscopic identification in the reflected light is ra-

Table 1

X-ray pattern of francolite from Rudna mine

Francolite from Rudna mine, sample RG 365 Ag		Francolite from Nassau*	
<i>I</i>	d_{hkl}	<i>I</i>	d_{hkl}
1	5.27		
4	3.44	1	3.437
2.5	3.16	1	3.160
2.5	3.04	3	3.050
10	2.78	10	2.789
6	2.69	6	2.694
3	2.63	3	2.622
1	2.50	1	2.507
2	2.28	1	2.289
4	2.24	2	2.242
1	2.13	1	2.131
1	2.06	1	2.067
1	2.009	1	2.026
6	1.934	3	1.931
2	1.877	1	1.880
5	1.839	3	1.836
2	1.796	2	1.795
1.5	1.766	2	1.764
1.5	1.735	2	1.745
1	1.637	1	1.632
1	1.574		
1	1.522	1	1.528
1	1.500		
2	1.463	2	1.465
2	1.452	1	1.452
1	1.422	2	1.420

* Grunner and McConnel (1937).

ther difficult. The mineral is isotropic with low reflectivity corresponding to the R_{\max} of dolomite. Occasionally, it shows typical features of amorphous substances. Despite its transparent character, internal reflections are rarely visible. If so, these are whitish in colour (for francolites free from organic compounds). When examined in transmitted light the mineral is usually brown to yellowish-brown and isotropic.

X-ray studies revealed the presence of francolite — $\text{Ca}_{10}(\text{PO}_4)_6 [\text{F}_2, (\text{OH})_2, \text{CO}_3, \text{O}]$. The reflections obtained are in good agreement with the data by Gruner and McConnel (1937) (Tab. 1).

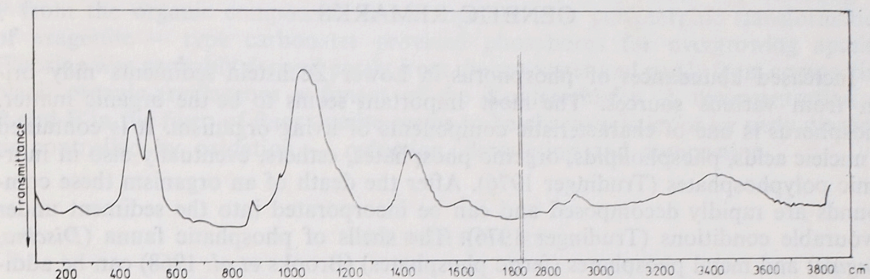


Fig. 1. Infrared spectrum of francolite from Rudna mine, sample RG 365 Ag

More detailed information has been provided by infrared spectrum (Fig. 1). The absorption bands suggest the mineral to be the fluorine-bearing apatite containing some amounts of CO_3^{2-} anions substituting for PO_4^{3-} ones. γ_3 vibrations of the PO_4 groups are responsible for the peaks 1055, 1078 and 1095 cm^{-1} whereas γ_4 ones cause the peaks 573, 578 and 606 cm^{-1} . The substituting CO_3 groups are documented by the presence of 870, 1430 and 1458 cm^{-1} bands. Traces of OH^- anion cause a weak absorption in 1545 cm^{-1} band which corresponds to the valence vibration of OH^- group. Its position may be also occupied by F^- and/or Cl^- ions. It is in agreement with 1 to 2 wt% F determined in phosphates from the Kupferschiefer (Kucha, Pocheć 1983). Absorption in the range of 2800—3000 cm^{-1} suggests the occurrence of organic aliphatic compounds (resins?) which presumably causes the brownish colour of francolite observed in the transmitted light. This band originates from the valence vibrations of CH_2 and CH_3 groups.

MICROSCOPIC STUDIES

In Rudna mine francolite was found mainly in the samples from dolomitic shale and argillaceous dolomite (lowermost part of Zechstein kalk sequence). Occasionally, it was also found in the top part of Weissligendes sandstone near the boundary with the shale. Local enrichments in phosphorus mineral have been observed in the lead- and zinc-bearing shales, in the NE slope of Rudna elevation zone.

Typical forms of francolite occurrence are elongated lenses, usually cracked. The cracks may be filled with calcite showing dark internal reflections or with sulphides. Francolite usually replaces the fossil remnants e.g. algae (Phot. 1), fills the fragments of brachiopods and other, unidentified organic relics (spores?) (Phot. 2, 3). It may also form elongated lenses partly replaced by chalcocite (Phot. 4). In the dolomitic shale lensoidal structures were observed (Phot. 5) in which the central part is occupied by crushed slabs of francolite embedded in a minute intergrowths of sphalerite

and also chalcocite or galena. The cracks are usually filled with sulphides of later generation. Sporadically, small amounts of bornite, chalcopyrite and/or calcite were also observed. The forms described above are sometimes surrounded by organic matter.

It should be noted, that a mineral showing optical properties identical as francolite has been observed in samples from the top part of Lower Zechstein copper-bearing marls in Konrad mine (North Sudetic Syncline). This phosphate replaces fossil remnants and is associated with calcite.

GENETIC REMARKS

Increased abundances of phosphorus in Lower Zechstein sediments may originate from various sources. The most important seems to be the organic matter. Phosphorus is one of characteristic components of living organism. It is contained in nucleic acids, phospholipids, organic phosphates, esters, eventually also in inorganic polyphosphates (Trudinger 1976). After the death of an organism these compounds are rapidly decomposed and can be incorporated into the sediment under favourable conditions (Trudinger 1976). The shells of phosphatic fauna (*Discina*, *Lingula*) and metal phosphates (ferric phosphates) (Brooks *et al.* 1968) can be additional sources of this elements. According to Brooks *et al.* (1968) interstitial solutions of sediments originated in reducing environment may be supersaturated in relation to phosphates. In the presence of high content of CO₂ derived from the decomposition of organic matter and excess of Ca²⁺ minerals of apatite group may precipitate even more readily than calcite (Brooks *et al.* 1968). Kramer (1964) considers Ca-fluorapatite to be a stable phase under conditions of pH below 7.8, temperature 10°C and phosphate ion concentration 10⁻⁶ M. One of the possible mechanisms of decomposition of organic matter is autoxidation. Kucha (1981, 1982) characterised some details of this process in Lower Zechstein metal-bearing shales. This author suggests that phosphates are in close genetic relation to gold and platinum-group elements enriched in some small areas in the Lubin copper district. Phosphates played the role of "coagulator" which formed insoluble or soluble complexes with noble metals-organic complexes (Kucha 1982).

CONCLUSIONS

It is accepted that Ca-phosphates are formed as a chemical precipitate at pH between 7 to 7.8 (Narębski 1960; Polański, Smulikowski 1969). Living organisms such as plankton, brachiopods, foraminifers and algae can be considered as a possible source of P in the Kupferschiefer environment. Marine organisms concentrate P present in the sea water to produce skeleton and incorporating P into proteins and enzymes (Businski 1937, 1938, 1952, 1954-*vide* Narębski 1960; Polański, Smulikowski 1969).

One of possible fluorine sources are volcanic exhalations. Such sources was suggested for fluor-apatites found in Carpathians (Narębski 1960). However, fluorine detected in the apatites present in the Kupferschiefer cannot be considered as a volcanic — exhalative because no volcanic activity was detected in the mineralized Zechstein. The most probable source of F may be pore waters of argillaceous sediments and algal mats (Fuchs 1981). The concentration of fluorine in argillaceous sediments may be as high as 1300 ppm (Turekian, Wedepohl 1961). An average F concentration in the sea water is about 1 ppm. Due to sorption and diagenetic chan-

ges a concentration of F in pore waters may be strongly increased. In the reef environment (Fuchs 1981) F is connected with the Mg²⁺ ion as complex MgF⁺. Dolomitisation removes Mg from this complex into the solid state and a freed F may stay in the solution or may be precipitated as CaF₂ or may be incorporated into the structure of apatite. Both discussed Ca minerals are present in the Kupferschiefer environment (Füchtbauer 1958; Kucha, Pocheć 1983). Apatite in carbonate sections covers surfaces of cavities and forms banded infilling cements together with glauconite (Kucha, Pocheć 1983). It suggests that apatite was formed in at early diagenesis in a subsurface environment close to the sea floor.

Oxidation — reduction reactions were probably responsible for releasing of P from the organic compounds which together with polymorphic transformation of aragonite — type carbonates provided phosphorus for overgrowing apatite. Fluorine was probably derived partly from the sea-water and partly from compacting black organic-argillaceous sediment of the Kupferschiefer. A reconcentration of P and F in the form of fluor-apatite seems to be characteristic for an early diagenesis controlled by oxidation — reduction, dewatering and compaction.

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FRANKOLIT Z UTWORÓW DOLNEGO CECHSZTYNU
MONOKLINY PRZEDSUDECKIEJ (KOPALNIA RUDNA)

Streszczenie

Apatyt fluorowy (frankolit) napotkano w najniższej części utworów węglanowych cechsztynu, tj. w łupkach dolomitycznych, dolomitach ilastych, a niekiedy także w stropowej części piaskowców białego spagowca. Zawartość apatyту fluorowego wzrasta w łupkach cynkonośnych. Frankolit zastępuje zwykle resztki skamieniałości (algi, ramienionogi i in.). Sugeruje to biogeniczne pochodzenie frankolitu utworzonego z fosforu, który został uwolniony z substancji organicznych w wyniku ich autooksydacji.

OBJAŚNIENIE FIGURY

Fig. 1. Widmo absorpcyjne w podczerwieni frankolitu z kopalni Rudna, próbka RG 365 Ag

OBJAŚNIENIA FOTOGRAFII

Plansza I

- Fot. 1. Struktura przypominająca algi zastępowane przez frankolit (*fr*). Wewnątrz frankolitu widoczne są małe inkluzje siarczków miedzi. Część środkowa wypełniona jest chalkozynem (*cc*) i bornitem (*bn*). Kopalnia Rudna, próbka RG 86/6, światło odbite
- Fot. 2. Struktura przypominająca zęby ryby zmineralizowane chalkozynem (*cc*) i frankolitem (*fr*) w dolomicie ilastym. *om* — substancja organiczna. Kopalnia Rudna, próbka RZ 34/12, światło odbite
- Fot. 3. Forma organiczna zbudowana z frankolitu i chalkopirytu (*cp*) w łupku ilastym. Kopalnia Rudna, próbka Po-8 142 Ag/c, światło odbite.

Plansza II

- Fot. 4. Chalkozyn (*cc*) zastępujący szczątki skamieniałości zbudowany z frankolitu (*fr*), w piaskowcu najwyższej części białego spagowca, o spoiwie ilasto-węglanowym. Kopalnia Rudna, próbka RG 43/14, światło odbite
- Fot. 5. Fragment soczewki zbudowanej z subtelných przerostów sfalerytu (*sp*) i frankolitu. Szczątki organiczne (alga?) w obrębie soczewki są zastąpione przez frankolit (*fr*). Kopalnia Rudna, próbka RG 58/9, światło odbite

ФРАНКОЛИТ ИЗ НИЖНЕЦЕХШТЕЙНОВЫХ ОБРАЗОВАНИЙ
ПРЕДСУДЕТСКОЙ МОНОКЛИНАЛИ (РУДНИК „РУДНА”)

Резюме

Фторapatит (франколит) встречен в низах карбонатных образований цехштейна, т.е. в доломитовых сланцах, глинистых доломитах, а иногда в кровельной части песчаников белого лежня. Содержание фторapatита увеличивается в цинконосных сланцах. Франколит замещает обычно остатки окаменелостей (альги, брахиоподы и др.). Это указывает на биогенное происхождение франколита, образованного из фосфора, который освободился с органического вещества в итоге его автооксидации.

ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. ИК-спектр поглощения франколита из рудника "Рудна", образец RG 365 Ag

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Таблица I

- Фото 1. Структура, напоминающая замещаемые франколитом (*fr*) альги. Внутри франколита заметны тонкие включения сульфидов меди. Центральная часть выполнена халькозином (*cc*) и борнитом (*bn*). Рудник "Рудна", образец RG 86/6, отраженный свет
- Фото 2. Структура в глинистом доломите, напоминающая минерализованные халькозином (*cc*) и франколитом (*fr*) зубы рыб. *om* — органическое вещество. Рудник "Рудна" образец RZ 34/12, отраженный свет
- Фото 3. Органическая форма, сложенная франколитом и халькопиритом (*cp*) в глинистом сланце. Рудник "Рудна", образец Po-8 142 Ag/c, отраженный свет

Таблица II

- Фото 4. Халькозин (*cc*), замещающий остаток окаменелости, сложенной франколитом (*fr*) в песчанике верхов белого лежня с глинисто-карбонатным цементом. Рудник "Рудна", образец RG 43/14, отраженный свет
- Фото 5. Фрагмент линзы, сложенной тонкими сростаниями sfalerита (*sp*) и франколита. Органические останки (альги?) в границах линзы замещены франколитом (*fr*). Рудник "Рудна", образец RG 58/9, отраженный свет

Plate I

- Phot. 1. Algae-like structure replaced by francolite (*fr*). Inside francolite a minute inclusions of Cu-sulphides are visible. Central part is filled by chalcocite (*cc*) and bornite (*bn*). Rudna mine, sample RG 86/6, reflected light
- Phot. 2. Structure resembling teeth of fish mineralized by chalcocite (*cc*), francolite (*fr*) and organic matter (*om*) in argillaceous dolomite. Rudna mine, sample RZ 34/12, reflected light
- Phot. 3. Organic form composed of francolite and chalcopyrite (*cp*) in clay shale. Rudna mine, sample Po-8 142 Ag/c, reflected light

Plate II

- Phot. 4. Chalcocite (*cc*) replacing a fossil remnant composed of francolite (*fr*) in sandstone, top-most part of the Weisslegendes, clay-carbonate cement. Rudna mine, sample RG 43/14, reflected light
- Phot. 5. Fragment of a lens composed of minute intergrowth of sphalerite (*sp*) and francolite. Organic fragment (algae?) within the lens are replaced by francolite (*fr*). Rudna mine, sample RG 58/9, reflected light

