Apatite in coal from bed 361 in the south-western part of the Upper Silesian Coal Basin

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Abstract. The presence and form of occurrence of phosphorus in coal is important not only from the scientific point of view, but it is also relevant in practical aspects (origin of deposit, paleoenvironment index, correlation of beds, coke production, economically significant presence of REEs in phosphates). In the south-western part of the Upper Silesian Coal Basin, in coal bed 361, sampled in one of the mines, phosphorus occurs in the form of its phase - apatite, which accompanies kaolinite, siderite, dolomite and pyrite. Apatite contains significant amounts of fluorine, which allows the mineral to be classified as fluorapatite. In the examined apatites Ca was substituted by Na, Mn and REEs, and P was substituted by Si. The presence of fluorapatite alongside kaolinite, as well as the idiomorphic form of occurrence of fluorapatite, indicate that this mineral is an automorphic component of coal which formed during the metamorphism of organic matter.

1. Introduction

Apatite is the most common phosphorus-bearing mineral component in coal, and phosphorus is an undesirable element in coal, particularly in coal used for coke production. Other mineral components that bring phosphorus into coal include goyazite-gorceixite-crandallite aluminophosphates, and florencite, monazite and xenotime series. These minerals have been found in hard coals in Polish coal basins [1, 2, 3] and in the ashes of such coals [4, 5]. However, the presence of phosphorus in coal also depends on the content of that element in the plants from which coal was formed and on the course of the process of diagenesis [6].

The presence and form of occurrence of phosphorus in coal is important not only from the scientific, but also from the practical point of view. This is because [7]:

- phosphorus present in apatite or in goyazite-gorceixite is an important factor in the economic evaluation of coal used for metallurgical purposes (e.g. coking coal) due to the possibility of undesirable reactions between P and Fe during the iron-making process;
- both apatite and goyazite-gorceixite can contain significant amounts of rare earth elements of potential economic value;
- apatite is in some cases a mineral that indicates the pyroclastic origin of the material in a boggy environment, particularly when tonsteins are present in the coal bed;
- the presence of goyazite-gorceixite minerals in coal layers is often treated as a proof of volcanic origin;
• in some coal beds high phosphorus content may be used for stratigraphic correlation;
• phosphorus minerals may be used as indices of the properties of sedimentary environments during the formation of peat, such as pH, redox potential, etc.

The occurrence of phosphorus in Polish coal was the subject of studies of coal from the south-western part of the Upper Silesian Coal Basin (USCB) [8, 9, 10].

This work focuses on the determination of the forms of phosphorus occurrence in coal of bed 361 in one of the coal mines in the south-western part of USCB.

2. Sampling and methods
The study was based on a channel sample taken from coal seam 361 at 681 m below sea level in accordance with PN-ISO 13909. The sample was taken in one of the mines in the south-western part of the Upper Silesian Coal Basin (figure 1).

Figure 1. Location of the area of study in the main geological zone in the Upper Silesian Coal Basin (Poland). Symbols: 1 – metamorphic rocks. DEVONIAN: 2 – carbonate and clastic marine sediments. CARBONIFEROUS: Namurian A – Upper Viséan: 3 – diastrophic marine sediments. Namurian A: 4 – Paralic Series. Namurian B + C: 5 – Upper Silesian Sandstone Series. Westphalian A + B: 6 – Siltstone Series. Westphalian C + D: Cracow Sandstone Series: 7 – Łaziska layers, 8 – Libiąż layers. Stephanian: 9 – Kwaczała Arkose. 10 – main faults, 11 – Carpathian overthrust (according to [11], modified).
In order to determine the mineral composition of the coal, the sample was ground to particle size \( \phi < 0.1 \text{ mm} \) and it was cleaned in a tetrachlorethylene-toluene mixture with a density of \( d=1.40 \text{ g cm}^{-3} \). The \( d>1.40 \text{ g cm}^{-3} \) fraction was subjected to an X-ray phase analysis on a PANalytical Empyrean diffractometer. Cu-K\( \alpha \) radiation was used. The X-ray diffraction patterns were recorded within the angle range 2\( \theta \) of 5° to 70° using an step interval of 0.02°, during the time of 2 seconds. The content of identified mineral phases was determined by quantitative diffraction analysis using the Rietveld method and SiroQuant® Version V3.0 computer software.

Precise identification of the phosphorus-containing mineral components was performed using electron scanning microscopy with chemical composition determination in micro areas (SEM SU3500 microscope from Hitachi coupled with a NORAN System 7 EDS UltraDry energy-dispersive X-ray spectrometer from Thermo Scientific). 7 to 10 measurements were made on each grain.

3. Results

Detailed characteristics of maceral and chemical composition of the analyzed coal sample, including content of rare earth elements, were presented in other papers [11, 12]. It was then found that the tested coal sample contained 5.06 wt% and 1.61 wt% phosphorus (P\( _2 \)O\( _5 \)), and the coal was classified as medium rank B (meta bituminous), vitrinite-rich coal (ECE Geneva 1998).

Phase identification by X-ray diffraction revealed that the main components of the sample after gravity separation in a mixture of tetrachlorethylene and toluene were (figure 2): siderite, dolomite, kaolinite, apatite and pyrite. The high background intensity of X-ray diffraction patterns in the 2-theta range of 8 to 30° indicates the presence in the sample of a significant amount of amorphous substance, which in this case is organic matter.

![Figure 2](image-url)  
**Figure 2.** X-ray diffraction pattern of coal sample (coal seam 361, level – 682m under the sea level) after enrichment in a mixture of tetrachlorethylene and toluene: S – siderite, D – dolomite, K – kaolinite, A – apatite, P – pyrite.

The dominating mineral component of the sample was kaolinite, its content exceeding 46% (table 1). The second most abundant component included minerals of the carbonate group, represented by
siderite and dolomite, their total content being close to 40%. The content of pyrite was ca. 9%, whereas that of apatite was less than 5%.

Morphology of apatite grains examined by scanning electron microscopy revealed the presence of three forms of this mineral. Most of the grains observed had irregular shapes (figures 3 and 4), less frequent were idiomorphic capillary and columnar crystals (figures 5 and 6). Sharp edges and interpenetrating crystals were observed even in irregular grains. These grains had no detrital nature.

**Table 1.** Mineral content in the coal sample (coal seam 361, level – 682m under the sea level) after enrichment in a mixture of tetrachlorethylene and toluene (in%).

| Mineral | Content |
|---------|---------|
| Siderite | 28.6    |
| Dolomite | 11.3    |
| Kaolinite | 46.3   |
| Apatite | 4.7     |
| Pyrite | 9.1     |

**Figure 3.** Irregular grain of apatite, SEM image.

**Figure 4.** Irregular grain of apatite, SEM image.

**Figure 5.** Capillary crystal of apatite, SEM image.

**Figure 6.** Columnar crystal of apatite, SEM image.
The chemical composition of the examined apatite grains included the main components typical for this mineral, i.e. CaO and P₂O₅, the content of which varied in the ranges of 49.46 to 55.19 wt% and 33.99 to 37.83 wt%, respectively (tables 2 and 3).

**Table 2.** Chemical composition of apatite from coal sample (coal seam 361, level – 682m under the sea level) after enrichment in a mixture of tetrachlorethylene and toluene (in %). Morphology: I-irregular shapes, Cp-idiomorphic capillary, Co-idiomorphic columnar.

| Chemical constituent | Measurement point number and morphology |
|----------------------|----------------------------------------|
|                      | 1     | 1-pt2 | 1-pt3 | 1-pt4 | 1-pt5 | 1-pt6 | 1-pt7 | 1-pt8 | 1-pt9 |
| CaO                  | 55.19 | 53.58 | 53.75 | 49.46 | 53.52 | 52.89 | 53.59 | 50.73 | 50.29 |
| Na₂O                 | 0.20  | 0.43  | 0.28  | 0.60  |       |       |       |       |       |
| MnO                  | 0.04  | 0.06  | 0.14  | 0.15  | 0.12  |       |       |       |       |
| MgO                  | 0.52  | 0.78  | 0.66  | 1.30  | 0.61  | 0.63  | 0.41  | 0.98  | 0.94  |
| La₂O₃                | 0.66  | 0.71  |       |       | 1.24  | 1.25  | 0.28  |       | 0.66  |
| Ce₂O₃                | 0.54  | 0.86  | 2.26  |       | 0.87  | 1.18  | 0.97  |       | 1.69  |
| Pr₂O₃                | 0.51  | 0.32  | 0.53  | 0.28  | 0.95  | 1.14  |       |       | 1.35  |
| Nd₂O₃                | 0.66  | 0.48  | 0.54  | 0.77  | 1.47  | 0.15  | 0.85  | 0.00  |       |
| Sm₂O₃                | 0.00  | 0.16  | 0.70  | 1.06  | 0.28  |       | 0.65  |       | 1.05  |
| Gd₂O₃                | 1.83  | 0.74  | 0.29  | 0.98  |       | 0.75  |       |       | 1.07  |
| ThO                  | 0.24  | 0.18  |       |       |       |       |       | 0.07  |       |
| P₂O₅                 | 36.76 | 36.17 | 36.25 | 33.99 | 37.83 | 37.49 | 37.39 | 34.98 | 35.42 |
| SiO₂                 | 1.39  | 2.18  | 2.71  | 4.30  | 0.60  | 1.05  | 0.61  | 2.46  | 3.15  |
| Cl                   |       |       |       |       |       |       |       |       | 0.57  |
| F                    | 3.20  | 3.72  | 3.47  | 5.59  | 4.24  | 4.37  | 4.47  | 5.19  | 5.38  |
| Total                | 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00| 100.00|

**Table 3.** The number of ions in the examined apatite grain in the tested coal sample (coal seam 361, level – 682m under the sea level) after enrichment in a mixture of tetrachlorethylene and toluene calculated as 25 (O, F, Cl, OH), 16 cations.

| Element | Measurement point number |
|---------|--------------------------|
|         | 1-pt1 | 1-pt2 | 1-pt3 | 1-pt4 | 1-pt5 | 1-pt6 | 1-pt7 | 1-pt8 | 1-pt9 |
| Ca      | 9.48  | 9.24  | 9.25  | 8.75  | 9.35  | 9.27  | 9.41  | 9.08  | 8.96  |
| Na      | 0.06  | 0.14  | 0.09  | 0.19  |       |       |       |       |       |
| Mn      | 0.01  | 0.02  | 0.02  | 0.02  |       |       |       |       |       |
| Mg      | 0.12  | 0.19  | 0.16  | 0.32  | 0.15  | 0.15  | 0.10  | 0.24  | 0.23  |
| ΣREE    | 0.14  | 0.17  | 0.17  | 0.27  | 0.18  | 0.21  | 0.29  | 0.29  | 0.29  |
| Th      | 0.01  | 0.01  |       |       |       |       |       |       |       |
| P       | 4.99  | 4.93  | 4.93  | 4.75  | 5.22  | 5.19  | 5.19  | 4.95  | 4.99  |
| Si      | 0.22  | 0.35  | 0.44  | 0.71  | 0.10  | 0.17  | 0.10  | 0.41  | 0.52  |
| Cl      |       |       |       |       |       |       |       | 0.16  |       |
| F       | 1.62  | 1.89  | 1.76  | 2.92  | 2.19  | 2.26  | 2.32  | 2.74  | 2.83  |
| OH      | -0.66 | -0.92 | -0.79 | -1.92 | -1.20 | -1.27 | -1.33 | -1.89 | -1.83 |
| Total   | 16.00 | 16.00 | 16.00 | 16.00 | 16.00 | 16.00 | 16.00 | 16.00 | 16.00 |

Fluorine content, varying between 3.20 and 5.59 wt%, was strikingly high, while chlorine was found in one grain only (0.57 wt%) (grain 1-pt8).

Silica content ranged from 0.60 to 4.30 wt%, while that of magnesium ranged from 0.41 to 1.40 wt%.
An important quantitative component of the examined apatite grains were rare earth elements (REEs), as the content of some of them exceeded 2 wt% (cerium in grain 1_pt4). More important, however, is the total content of rare earth elements (ΣREE), which ranged from 2.49 (grain 1_pt1) to 4.87 wt% (grain 1_pt8).

The content of other chemical components is of little importance, although the content of Na₂O is noteworthy, as grains were found in which the content of this component was in the range of 0.20 to 0.60 wt% (grains 1_pt1 - 1_pt4) and there were also grains in which this component was not detected at all (grains 1_pt5 - 1_pt9). It is interesting that slightly higher ΣREE content (above 3 wt%) was determined in grains in which no Na₂O was found in comparison to grains in which Na₂O presence was detected (usually below 3 wt% ΣREE).

Neither strontium, iron or yttrium were found in the examined apatite grains (content below the limit of detection).

4. Discussion

The research show that the chemical composition of the examined apatite grains does not show any relation to the morphology of this mineral. It seems, however, that such a conclusion should be supported by a study of a larger number of apatite grains in a larger number of various coal samples.

The value of the correlation coefficient for Ca atoms per formula unite (a.p.f.u.) and P (a.p.f.u.) content is 0.69. However, when one considers two groups of apatite grains formed according to their Na₂O content, it can be seen that the correlation for grains where Na₂O is present takes the value 1.00, and for the second group (with no Na₂O) it takes the value 0.90, which for the linear type of trend results in high values of R², 0.99 and 0.82, respectively (figure 7).

![Figure 7. Variability of Ca (a.p.f.u.) and P (a.p.f.u.) content in the tested apatite grains.](image-url)

There is a distinct correlation between Ca atoms per formula unite (a.p.f.u.) and Mg (a.p.f.u.), equal to -0.97, which for the linear type of trend gives a high value of R² = 0.93 (figure 8). The most probable assumption is that magnesium substitutes calcium in the structure of this mineral.
Figure 8. Variability of Ca (a.p.f.u.) and Mg (a.p.f.u.) content in the tested apatite grains.

The value of the correlation coefficient for Ca (a.p.f.u.) and $\sum$REE (a.p.f.u.) content is high at -0.81. However, when one considers two groups of apatite grains formed according to their Na$_2$O content, it can be seen that the correlation for grains where Na$_2$O is present takes the value -0.99, and for the second group (with no Na$_2$O) it takes the value -0.88, which for the linear type of trend results in high values of $R^2$, 0.99 and 0.78, respectively (figure 9).

Figure 9. Variability of Ca (a.p.f.u.) and $Y+\sum$REE (a.p.f.u.) content in the tested apatite grains.

There is an interesting relationship between fluorine content and $\sum$REE. With increasing F content, the content of rare earth elements also clearly increases. The value of the correlation coefficient for the content of these components is high at 0.96. For the linear type of trend the value of $R^2$ is 0.93 (figure 10).
Figure 10. Variability of F and \( \sum \text{REE} \) content in the tested apatite grains.

There is also a distinct correlation between Si (a.p.f.u.) and P (a.p.f.u.), equal to -0.91, which for the linear type of trend gives a high value of \( R^2 = 0.93 \) (figure 11). The most probable assumption is that Si substitutes P in the structure of this mineral.

Figure 11. Variability of Si (a.p.f.u.) and P (a.p.f.u.) content in the tested apatite grains.

The studies show that the tested apatite grains belong to fluorine apatites, where only one grain was found to contain small amounts of chlorine. The general chemical formula of apatite group minerals is Ca\(_5\)(PO\(_4\))\(_3\)(OH,F Cl), where both calcium and phosphorus can be substituted by other specific elements [13, 14, 15, 16, 17]. In the examined apatite grains, Ca was substituted by Na, Mn and REEs, and P was substituted by Si.

Research shows that in coal seam phosphorus occurs mostly in the form of apatite. The probable source of phosphorus are phosphoproteins that are present in the primary organic matter of peat.
it is apatite or aluminophosphates (goyazite-gorceixite-crandallite) that are formed is probably determined mostly by factors such as pH and availability of metals [18]. At the same time the most common type of apatite that is present in coal beds is fluorapatite [19], which occurs alongside kaolinite. The presented results of examinations of apatite found in the described coal bed, in particular:

- occurrence of fluorapatite alongside kaolinite,
- idiomorphic form of fluorapatite occurrence,

indicate that this mineral is an automorphic component of coal which formed during the metamorphism of organic matter.

5. Conclusions

Based on the research performed, the following conclusions were drawn:

In the south-western part of the Upper Silesian Coal Basin, in coal seam 361, sampled in one of the mines, phosphorus occurs in the form of its phase - apatite, which accompanies kaolinite, siderite, dolomite and pyrite.

Apatite contains significant amounts of fluorine, which allows the mineral to be classified as fluorapatite. In this apatite Ca was substituted by Na, Mn and REEs, and P was substituted by Si.

The presence of fluorapatite alongside kaolinite, as well as the idiomorphic form of occurrence of fluorapatite, indicate that this mineral is an automorphic component of coal which formed during the metamorphism of organic matter.

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