Ammonium minerals from burning coal-dumps
of the Upper Silesian Coal Basin (Poland)

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Assemblages composed of 11 ammonium minerals, mainly sulphates and chlorides, were recorded from four burning coal-dumps (BCD) in the Upper Silesian Coal Basin. Most of them are newly recorded from Poland. Minerals were identified using PXRD and SEM with EDS analyses. Salammoniac, NH_4Cl, and tschermigite, $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ are the most common species on the BCD studied. Kremersite, $(NH_4,K)_2[FeCl_5(H_2O)]$, is rare and coexists with members of the ammonioalunite–ammoniojarosite series. Boussingaultite, $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, and more rarely clairite, $(NH_4)_2Fe_3(SO_4)_4(OH)_3 \cdot 3H_2O$, and mascagnite, $(NH_4)_2SO_4$, accompany numerous Mg, Al, Fe and Ca sulphate minerals. These usually occur as very fine admixtures forming coatings, small nodules or porous masses and were found on the BCD surface close to gas vents. Also a massive sulphate crust was found in the deeper part of the BCD nearby the fire zone. This crust is composed mainly of anhydrous sulphates: godovikovite, $(NH_4)(Al,Fe)(SO_4)_2$, and very minor sabieite, $(NH_4)Fe(SO_4)_2$, and efremovite, $(NH_4)_2Mg_2(SO_4)_3$, which were transformed into different hydrated sulphates in the outer zone of the crust. The fibrous or dendritic habit of many ammonium minerals, and the vesicular texture of some sulphate aggregates, point to their crystallization from the gas phase. Some ammonia minerals may also have developed through hydration of previously formed phases or precipitated from locally formed aqueous solutions due to cooling or evaporation. The appearance of ammonia minerals on BCD can be a useful indicator of the presence of underground fires.

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INTRODUCTION

Burning coal-dumps (BCD) have been recently the subject of intensive studies by different researchers, as they have become a serious problem in coalfields around the world. Coal waste piles are a persistent element of the landscape of almost all coal mining areas. Many of these are affected by fire and should be recognized as potentially hazardous for the natural environment (Panov *et al.*, 1999; Finkelman, 2004). BCD may emit serious amounts of gases, including such dangerous species as CO, SO_2, H_2S, NH_3, HCl, aromatic hydrocarbons and many others. They are also harmful pollutants for the atmosphere and soils by dispersing dust, and for ground water by the leaching of many toxic compounds and chemical elements.

Some burning processes on spoil-heaps can be of anthropogenic origin; however spontaneous combustion of the coal remnants initiated by self-ignition is considered to be the main cause. Ignition of the coal begins by accumulation of not less than 60–70% of the oxidation-derived heat, which is also dependent on the coal ash content (Srebrodolskiy, 1989). It is not yet fully understood whether the heat required for ignition is produced by oxidation of coal-disseminated pyrite, which is a common component of bituminous coal, or by the organic material itself. However, many authors (i.e., wi tosławski, 1953; Tvrdý and Sejkora, 1999) link the ignition with the maceral composition of the coal. Vitrite is the maceral of lowest ignition point and initiates ignition at around 300°C; meanwhile, the brittleness of fusite gives it a vast reactive surface. Pyrite is then regarded as an additional catalyst of the process, as its ignition temperature is around 330°C (Gryglewicz *et al.*, 1996). The progress of burning is accelerated by the access of atmospheric oxygen, due to moving of the dump material (subsidence, rubble flow) and intensified by rainfall-water, which plays an important role as an oxidation agent.

Burning of the dumps gives rise to the formation of many different mineral phases. We refer to these as true minerals although their appearance is associated with human activity. The environment, e.g., piles of mine waste materials, is built artificially but the rocks deposited and the mineral-forming processes are essentially similar to natural ones, known from certain geological environments. Among minerals originated on BCD, NH_4-bearing minerals are essential, as ammonium compounds are typical of BCD and are thought to be indicative of this environment. They are associated also with underground coal-mine fires and natural fires of exposed coal seams.

This paper presents the results of mineralogical investigations (XRD, SEM) used to identify and characterize assemblages that include the ammonium sulphate and chloride minerals derived from selected BCD in the Upper Silesian Coal Basin. The mineralogy of these BCD has been poorly known so far and most of the minerals found in this study have not previously been known from these localities, nor from Poland in general.

MINERAL ASSEMBLAGES GENERATED ON BCD

BCD are an environment for the formation of mineral assemblages very different from those typical of magmatic, thermal-metamorphic, volcanic exhalation and supergene processes. The burning-induced mineral-forming processes comprise the thermal transformation of waste-rocks or even their melting, coal gasification and carbonization and alteration of the waste-rocks by coal-derived fluids, and the condensation and crystallization of fluids (Tvrdý and Sejkora, 1999; Sokol et al., 2005). The BDS environment is very dynamic, depending on the temperature and chemical composition of the waste materials. Vertushkov (after Srebrodolskiy, 1989) distinguishes three main mineral-forming stages; the burnout stage (BS), pseudofumarolic stage (PS) and supergene stage (SS).

The burnout stage (BS) is connected with the high temperature decomposition of pyrite-containing coal-bearing rocks in the inner part of the fire zone. Pyrite ignition temperature (ca. 330°C) is regarded as the lower temperature limit of BS. The upper limit reaches 1300°C, as reported by Sokol et al. (2002) on the basis of the melting of waste-rocks (sideritic rocks, carbonate clay rocks and mudstones) at BCD in the Chelyabinsk Coal Basin. The main products of this stage are so-called paralavas formed by crystallization of local mobile melts, metacarbonate slags after Fe-rich carbonate rocks and clinker-like metaargilites after slates. Interaction of the paralava-parental melts with dumped sedimentary waste-rocks leads to the formation of buchites. The mineral composition of newly formed rocks can be very complex, depending on the type of waste-rock. Its most common components include mullite and spinel (after clay minerals), portlandite, periclase, magnetite, hematite, Ca ferrites, magnesioferrite (after carbonates), the ellestadite-apatite series, melilite-gehlenite, olivines, Ca-rich pyroxenes and other Ca-rich silicates (Filippidis et al., 1996; Reifenstein et al., 1999; Ward, 2002; Sokol et al., 2005). Many different sulphide minerals and native elements are also reported to form at temperatures pertinent to BS (Nasdala and Pekov, 1993; Tvrdý and Sejkora, 1999; Kruszewski, 2006). From the temperature conditions and character of the minerals formed, the BS processes can be referred to as pyrometamorphism and are similar and comparable to magmatic and high temperature metamorphic activity. The so-called combustion metamorphism, comparable to the sanidinite facies of bituminous carbonate-rocks from the Hatrurim Basin, Israel, is an example of the natural analogue of high temperature BS processes (Gur et al., 1995). Minerals formed during BS are also known from carbonatite lavas (Wooley and Church, 2005), meteorites (Farrell et al., 2002) and industrial slags.

The pseudofumarolic stage (PS) is ascribed to a temperature range of 450–50°C. Mineral-forming processes in PS include both desublimation (condensation) of coal- and waste-rock-derived gaseous compounds and interaction of these compounds with the waste-rocks themselves. Emanating gases exploit cracks and reach the dump surface and atmosphere through vents. This phenomenon is very similar to that known from solfataric or fumarolic areas in active volcanoes and can be also compared with some hot spring activity, such as H_2SO_4-rich steam vents at The Geysers, California (type locality of ammonioalunite, Altaner et al., 1988). Pseudofumarolic vents on the BCD surface constitute a system of spots or of fissures up to tens of meters long. The chemical composition of the gaseous phase includes vapor of H_2O, N_2, CO_2, CO, H_2, CH_4 (and other hydrocarbons), NH_3, H_2S, SO_2, HCl, sometimes also traces of HF and HCN (Srebrodolskiy, 1989ł Tvrdý and Sejkora, 1999; Stracher et al., 2005). Some vents can be mineralized. Depending on the temperature and distance from the fire, they can be occluded by soot (lower temperature, carbonization gas emanation) or covered by the typical PS minerals — native sulphur and salammoniac. Both minerals are well known also from volcanic areas e.g., Vesuvius and Paricutín volcanoes. Elemental sulphur, derived from pyrite (or other sulphides), coal organic matter or more rarely from sulphate minerals, generally crystallizes though the condensation of S-bearing gaseous compounds in the range 90–130°C. Sulphur crystallizes as monoclinic rosickýite above 95.6°C and below this temperature becomes orthorhombic; however it is often found as a paramorphosis after the monoclinic phase. Sulphur can co-precipitate with salammoniac, but higher temperatures, up to 310°C, will favor salammoniac. A yellow (coloured by sulphur) variety of salammoniac crystallizes between 80 and 90°C, while a colorless type appears from 120°C. Salammoniac forms by the reaction of coal-derived NH_3 and HCl. An alternative source of nitrogen may be air. A typical mineral of the PS is also mascagnite, $(NH_4)_2SO_4$, (Srebrodolskiy, 1989).

The supergene stage (SS) concerns low-temperature crystallization from locally circulating solutions and hydration of certain previously formed minerals. This stage includes also the oxidation under ambient conditions of pyrite or of other sensitive phases present in the dump material. The products of these processes are similar to those of acid mine drainage and to minerals occurring in the oxidation zones of ore deposits. Combustion-derived H_2SO_4 can be an additional oxidising agent to atmospheric O_2. The input of combustion-derived sulphates complicates understanding of the genesis of many sulfate minerals found on BCD. Acid, chemically aggressive solutions containing H_2SO_4, CH_3COOH, CO_2 and other compounds interact with the waste

rocks and produce a wide range of secondary sulphate minerals, most of them being unstable crystallohydrates.

Observations of the classic sites of coal seam combustion sites in Ravat and Kuh-i-Malik areas, central Tajikistan (Srebrodolskiy, 1989; Nasdala and Pekov, 1993) point to a zonation in the formation sequence of minerals, depending on the temperature and activity of gases. In the central zone, at temperatures above 600°C, the fire totally consumed the coal, and buchite and possible sulfide minerals such as oldhamite are formed. In nearby central parts of the fire area a sulphate crust composed mostly of anhydrous Al sulphates (millosevichite, godovikowite *etc.*) is formed above 350°C among H_2SO_4-cloyed metaargillite. There are no vents here and the gases are kept inside this zone. If the gases migrate to the surface, several assemblages can form. From the gas compounds derived mainly from coal decomposition, sulphur, salammoniac and additional mascagnite and letovicite precipitate. The interaction of sulphur gases with rocks may lead to the formation of alunite, jarosite, anhydrite, gypsum, alunogen, halotrichite-pickeringite, tschermigite and other sulphates. Around low-temperature gas vents, sulphur, salammoniac, tschermigite, hematite, kremersite and sometimes gwihabaite condense. In the outermost and low-temperature (up to 60°C) zone liquid bitumens and, rarely, native selenium and organic minerals such as ravatite (natural phenanthrene) concentrate.

Ammonium minerals can form on BCD mostly during the pseudofumarolic stage. Some were formed also as a result of supergene processes. A list of ammonium minerals reported from BCD and related sites worldwide is compiled from literature data in Table 1.

MATERIALS

The mineral samples for this study were collected on selected BCD sites in the Upper Silesian Coal Basin (USCB) (Fig. 1). They include dumps in: Czerwionka-D bie sko and Łaziska near Katowice; Zabrze-Biskupice; Rybnik-Rymer and Rydułtowy of the Rybnik Coal Area. The huge, now inactive, dump at Łaziska is known under the name "Skalny". The USCB, the most important source of bituminous coal in Poland, has a mining area of *ca.* 1800 km², where 65 underground mines were active in the last decades of the last century. Structurally the USCB is a Variscan foreland basin, developed on the Precambrian Upper Silesian Massif. The depression is filled by Carboniferous deposits of cyclical molasse character with numerous coal beds. They are composed of paralic sediments — clastic and fitogenic rocks: conglomerates, sandstones, mudstones, claystones — and overlying continental limnic deposits of the Upper Silesian sandstone series, mudstone series and Kraków sandstone series. The mudstone series contains carbonate rocks represented mainly by spherosiderites. Pyrite and marcasite are the main sulphur species in USCB coals (Czapli ski and Smolka, 1998). The productive Carboniferous series are covered by Triassic, Miocene and Quaternary rocks.

METHODS

Samples for this study were collected over the last 5 years in different seasons and weather conditions. After collection, the mineral samples were packed into sealed plastic containers to retain their natural moisture. When possible, the temperature was measured around mineral segregations and gas vents, using an IR pyrometer.

In the laboratory the minerals were carefully separated under a stereomicroscope. For PXRD identification, samples were gently crushed in an agate mortar and quickly mounted on a *Bruker axs D5005* diffractometer at the Department of Soil Environment Sciences (Faculty of Biology and Agriculture, Warsaw Agriculture University). Measurement parameters were as follow: CuKα and CoKα radiation, graphite monochromator, continuous scan mode with 0.02 step, 1 s counting time, 40 kV voltage and 30 mA current. The *hkl*, *d* (measured) and peak intensity (I/I_o ratio) values of the standards were taken from a PDF (2005) Maint V. 11.0 database and juxtaposed with obtained data in Tables 2–4. Aliquots of some samples were also left for 2 months in open receptacles to test their possible instability and changes under ambient conditions and then were analyzed again.

The crystal morphology and genetic relations among minerals of the assemblages under study were observed on a *JSM-6380LA* scanning electron microscope (JEOL, Japan) in the Scanning Electron Microscopy and Microanalysis Laboratory (Faculty of Geology, University of Warsaw). The chemical composition of objects on SEM images was constrained with an EDS microanalyzer. Most minerals occur as intimate mixtures, which makes quantitative chemical analyses impossible to carry out.

OCCURRENCE OF AMMONIUM MINERALS ON BCD

SALAMMONIAC NH4Cl

Native ammonium chloride is the most common ammonium mineral reported from BCD worldwide. In Poland salammoniac has been reported so far from Nowa Ruda–Słupiec, Lower Silesia (Wielogórski *et al.*, 1975). On the BCD of Upper Silesia we have found this mineral at Łaziska, Czerwionka-D bie sko, Rybnik-Rymer and Rydułtowy, both as mono-mineral aggregates and in complex aggregates of several sulfate minerals. The occurrence of salammoniac was confirmed by PXRD analyses. The obtained *d*-spacing and relative intensity values are very close to the standard (Table 2).

Salammoniac aggregates from the "Skalny" dump at Łaziska weighed up to a few kilograms. They cemented fragments of red burnt-out argillites (Fig. 2A). The mineral occurs as compact and porous masses. Dendritic and stalactitic forms are also often found (Fig. 2B) and may be composed of clear microcrystals (Fig. 2C). Such forms were found at Łaziska, Rybnik-Rymer and Rydułtowy. Some of these have a somewhat fibrous habit. A botryoidal habit is relatively rare and was observed at Rybnik-Rymer. Other unusual forms include crab-pin-

Ammonium minerals known from BCD and related sites

Mineral	Chemical formula	Localities
Letovicite	$(NH_4)_3H(SO_4)_2$	Letovice, Radvanice, Czech Rep. (1); Freital, Germany (2); Kuh-i-Malik, Tajikistan (3); Witbank and Sasolburg coalfields, South Africa (4)
Mascagnite	$(NH_4)_2SO_4$	Lyukóbánya, Hungary (5); Kladno, Radvanice, Czech Rep. (6); Alsdorf (7), Freital (8) and Ronneburg, (9), Germany; Forestville, Pennsylvania (10); Kuh-i-Malik, Tajikistan (3); Donbas, Ukraine (11); Chelyabinsk Coal Basin, Russia (12); Witbank and Sasolburg coalfields, South Africa (4)
Efremovite	$(NH_4)_2Mg_2(SO_4)_3$	Chelyabinsk Coal Basin, Russia (3, 12); Ronneburg, Germany (9)
Godovikovite	$(NH_4)(Al,Fe)(SO_4)_2$	Chelyabinsk Coal Basin, Russia (13); Radvanice, Czech Rep. (1); Alsdorf (7), Ronneburg (9), Freital (8), Germany; Wuda coalfield, China (14)
Sabieite	$(NH_4)Fe(SO_4)_2$	Ronneburg, Germany (9)
Koktaite	$(NH_4)_2Ca(SO_4)_2 \cdot 6H_2O$	Ronneburg, Germany (9)
Mohrite	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	Alsdorf, Germany (16); Radvanice, Czech Rep. (17)
Boussingaultite	$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	Radvanice, Czech Rep. (17); Ronneburg, Germany (9); Chelyabinsk Coal Basin, Russia (3, 12)
Tschermigite	$(NH_4)Al(SO_4)_2 \cdot 12H_2O$	Lyukóbánya, Komló, Hungary (5); Alsdorf (7), Freital (8) and Ronneburg (9), Germany; Radvanice, Czech Rep. (17); Donbas, Ukraine (11); Chelyabinsk Coal Basin, Russia (12); Wuda coalfield, China (14); Kuh-i-Malik, Tajikistan (3)
Clairite	$(NH_4)_2Fe_3(SO_4)_4(OH)_3 \cdot 3H_2O$	Komló, Hungary (5)
Ammonioalunite	$(NH_4)Al_3(SO_4)_2(OH)_6$	Radvanice, Czech Rep. (17); Ronneburg, Germany (9)
Ammoniojarosite	$(NH_4)Fe_3(SO_4)_2(OH)_6$	Muttlkogel Mt., Austria (19)
Gwihabaite	NH_4NO_3	Kuh-i-Malik, Tajikistan (3)
Salammoniac	NH_4Cl	Nowa Ruda-Słupiec, Poland (20); Radvanice, Czech Rep. (6); Alsdorf (7), Ronneburg (9) and Oelsnitz (27), Germany; Lyukóbánya, Egercsehi, Hungary (5); La Ricamarie (25), France; Donbas, Ukraine (11); Wuda coalfield (14), Gulaben and Rujigou coalfield (21), China; Chelyabinsk Coal Basin, Russia (3,12); Kuh-i-Malik, Tajikistan (3); Witbank and Sasolburg coalfields, South Africa (4)
Kremersite	$(NH_4,K)_2[FeCl_5(H_2O)]$	Alsdorf, Germany (7); Chelyabinsk Coal Basin, Russia (3,12); Ravat, Tajikistan (26)
Cryptohalite	$(NH_4)_2[SiF_6]$	Radvanice, Czech Rep. (6); Shenandoah, Pennsylvania (28)
Bararite	$(NH_4)_2[SiF_6]$	Radvanice, Czech Rep. (6); Shenandoah, Pennsylvania (28)
Barberiite	$NH_4[BF_4]$	Radvanice, Czech Rep. (29)

(1) Žá ek and Ondruš (1998); (2) Witzke (1995); (3) Srebrodolskiy (1989); (4) Pone *et al*. (2007); (5) Szakáll and Jánosi (1995); (6) Sejkora *et al*. (2001); (7) Sindern *et al*. (2005); (8) Thalheim *et al*. (1991); (9) Witzke and Rüger (1998); (10) Finkelman and Mrose (1977); (11) Panov *et al*. (1999); (12) Sokol *et al*. (2005); (13) Jambor and Grew (1990); (14) Stracher *et al*. (2005); (16) Kolitsch and Brandstätter (2007); (17) Jírasek (2001); (19) Exel (1993); (20) Wielogórski *et al*. (1975); (21) Kuenzer *et al*. (2007); (25) Laurent (1995); (26) Nasdala and Pekov (1993); (27) Witzke (1996); (28) Finkelman (2004); (29) Tvrdý and Sejkora (2000)

cer-like ones (Fig. 2D). Euhedral salammoniac crystals are common on each BCD. They are generally small, rarely reaching 3 mm, but crystals up to 1 cm across were also found. Individuals are often rounded and possess only ill-defined faces. Well-developed crystals, including tetrahedra and cubes, occur sporadically (Fig. 2E). Their crystal faces often possess different structures (Fig. 2F) that may reflect dynamic conditions of their growth. A typical feature of the BCD salammoniac crystals is their elongation along the *c*-axis (Srebrodolskiy, 1989), which was also commonly observed at USCB sites. The elongation may be so well developed that the crystals acquire a needle-like habit and seem to be more monoclinic than isometric. Aggregates and crystals of salammoniac are usually colorless, rarely hued yellow or even brown due to admixtures of native sulfur or organic matter, respectively.

The temperatures measured around salammoniac segregations varied from air temperature (i.e. by already inactive vents) to about 280°C. In general, the BCD salammoniac has formed under pseudofumarolic conditions. Forms such as dendrites point to a mineral genesis by condensation of gases.
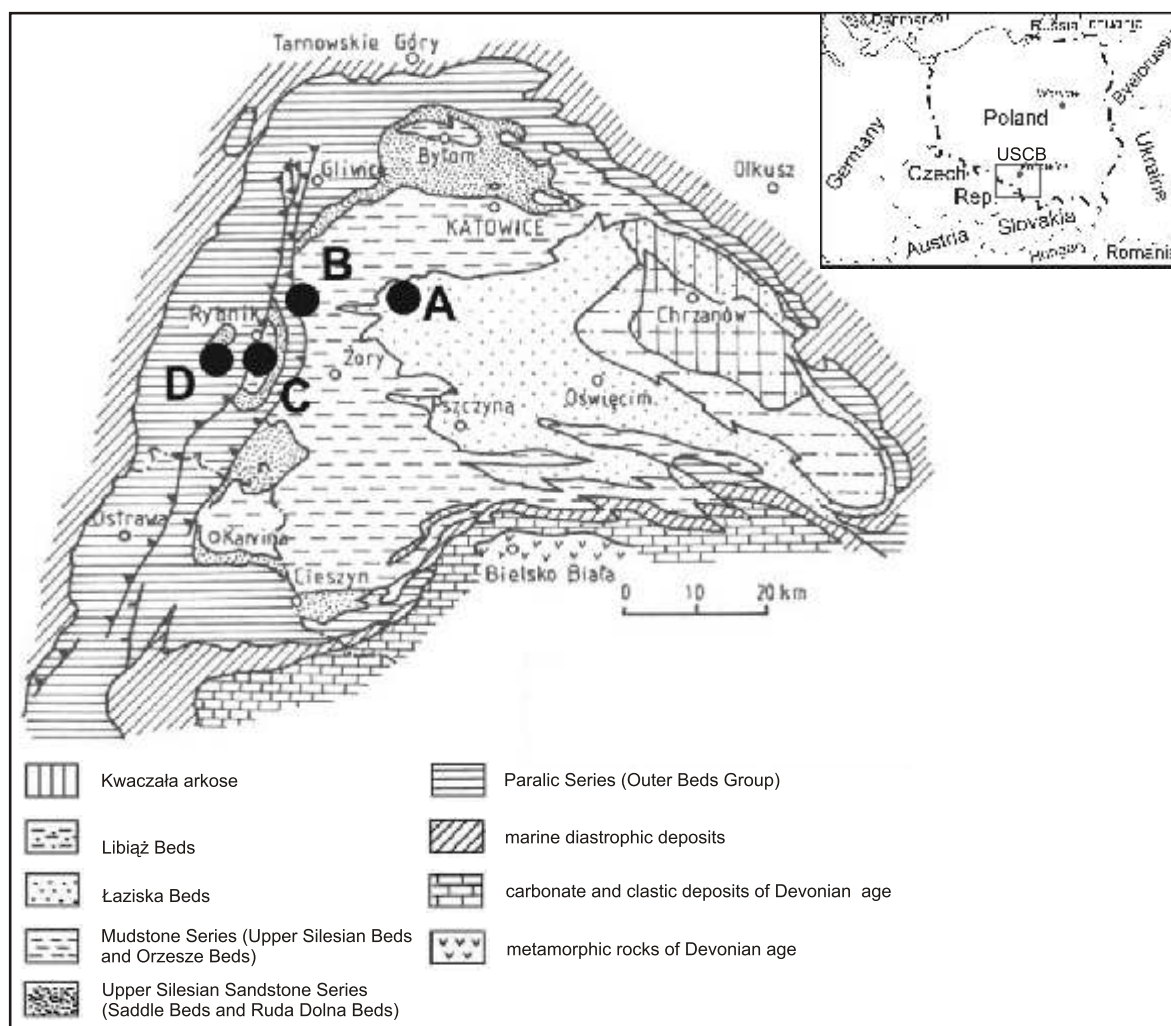
Fig. 1. Geological sketch-map of the Upper Silesian Coal Basin (after Gabzdyl, 1994)

Location of BCD studied: A — Łaziska ("Skalny" dump), B — Czerwionka-Dębieńsko, C — Rybnik-Rymer, D — Rydułtowy

T a b l e 2

X-ray powder diffraction data for salammoniac from the Upper Silesia BCD

Czerwionka-Dębieńsko sample		PDF 01-1043		
d (meas.) [Å]	I/I$_o$	d (meas.) [Å]	(I/I$_o$)	hkl
3.844	16	3.840	15	100
2.724	100	2.720	100	110
2.225	7	2.220	5	111
1.929	8	1.920	12	200
1.726	5	1.720	8	210
1.576	15	1.570	25	211
1.368	3	1.370	5	220

Salammoniac is often closely associated with native sulfur, as both minerals are thought to be formed from the gas phase. Some yellowish dendrites form fine intergrowths of these minerals. However, most of dendrites or massive forms are free of sulfur, suggesting a possible higher temperature of their formation. On the other hand, clusters of clear idiomorphic crystals could have precipitated from locally formed aqueous solution, probably at lower temperature, as a product of the recrystallization of former salammoniac aggregates.

KREMERSITE $(NH_4,K)_2[FeCl_5 \cdot H_2O]$

The natural ammonium (potassium) aquapentachloroferrate(III) is a rare sublimate mineral forming near volcanic fumaroles. Kremersite was described in 1851 from Vesuvius and named in 1853 for the German chemist Peter Kremers. The mineral was also reported as a subordinate constituent of BCD (see Table 1). In the Chelyabinsk Coal Basin, Southern Urals, it was described under the name *kopeyskite* (not accepted by the
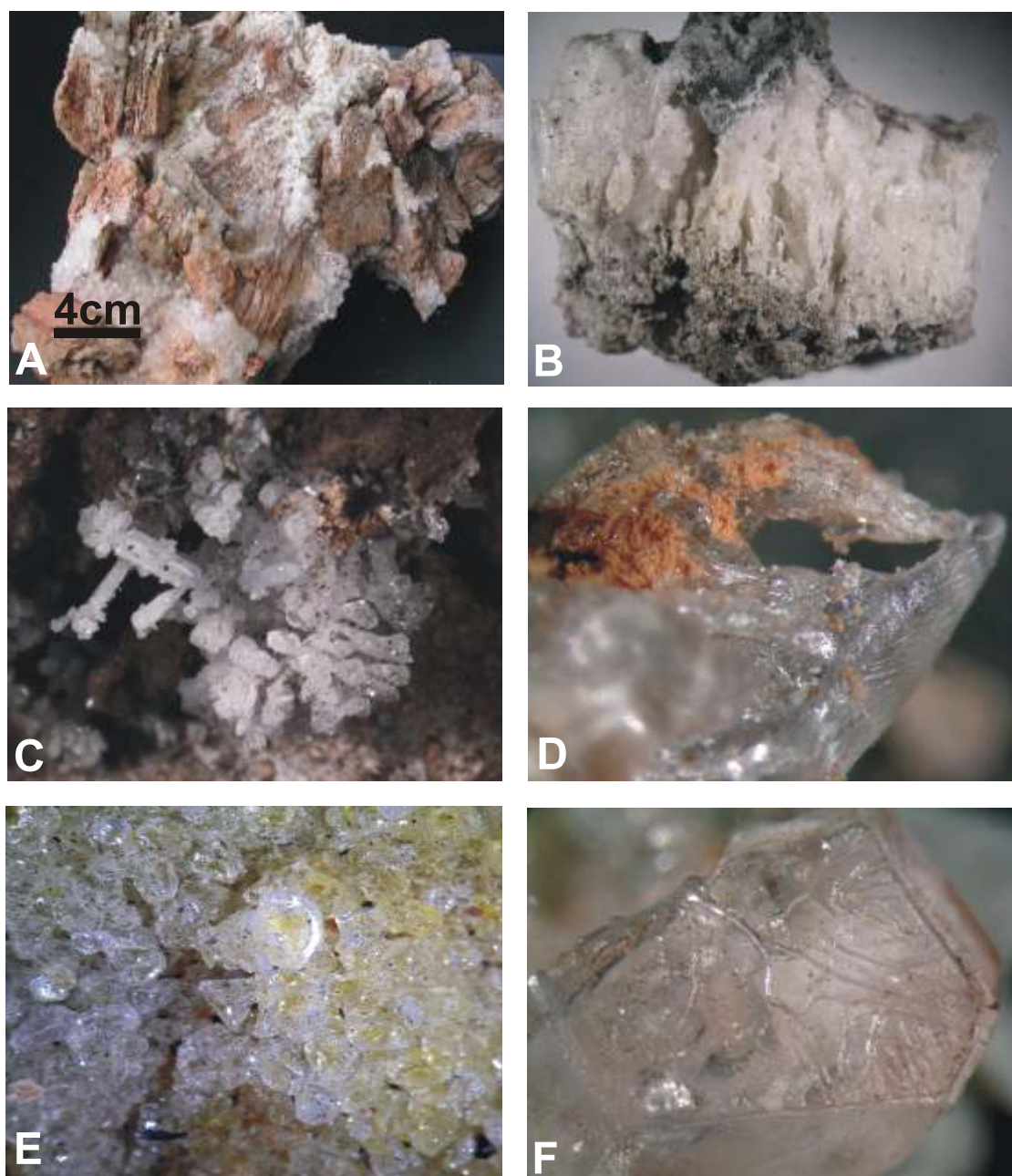
Fig. 2. Salammoniac aggregates and crystal habits from the Upper Silesian BCD

A — metaargilite fragments cemented by crystalline salammoniac, Łaziska; **B** — dendritic salammoniac aggregate, 3 cm wide, Rybnik-Rymer; **C** — elongated, often rounded salammoniac crystals forming a dendritic cluster 1.4 cm long, Rydułtowy; **D** — crab-pincer-like form of salammoniac, photo width 5.5 mm, Łaziska; **E** — well-developed salammoniac crystals with central tetrahedron *ca.* 1.5 mm wide on native sulfur, Rydułtowy; **F** — growth structure on 2.7 mm long salammoniac crystal face, Łaziska

IMA). We found this mineral on the Upper Silesian BCD in Czerwionka-Dębieńsko and identified it by the PXRD method (Fig. 3). This is the first record of kremersite in Poland. On the Silesian BCD, kremersite occurs sporadically as orange-red coatings (Fig. 4A) on NH_4-rich members of the alunite-jarosite series developed in the cover of the sulfate crust, which is composed mainly of godovikovite. It forms small aggregates of orthorhombic blades. Some kremersite aggregates also show a fibrous habit, visible on SEM images (Fig. 4B). The fibres are often curved. The fibrous habit suggests rapid deposition from the gas phase. Kremersite is very deliquescent and can persist only under favourable ambient conditions.

AMMONIOALUNITE–AMMONIOJAROSITE
$$(NH_4)Al_3(SO_4)_2(OH)_6–(NH_4)Fe_3(SO_4)_2(OH)_6$$
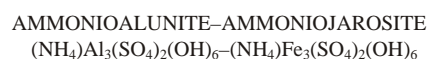
Ammoniojarosite, first described in 1927 from shale containing lignite and pyrite near the Kaibab Fault, Utah, USA, is an uncommon constituent of oxidation zones of pyritic rocks rich in organic material (Odum *et al.*, 1982). Ammonioalunite,
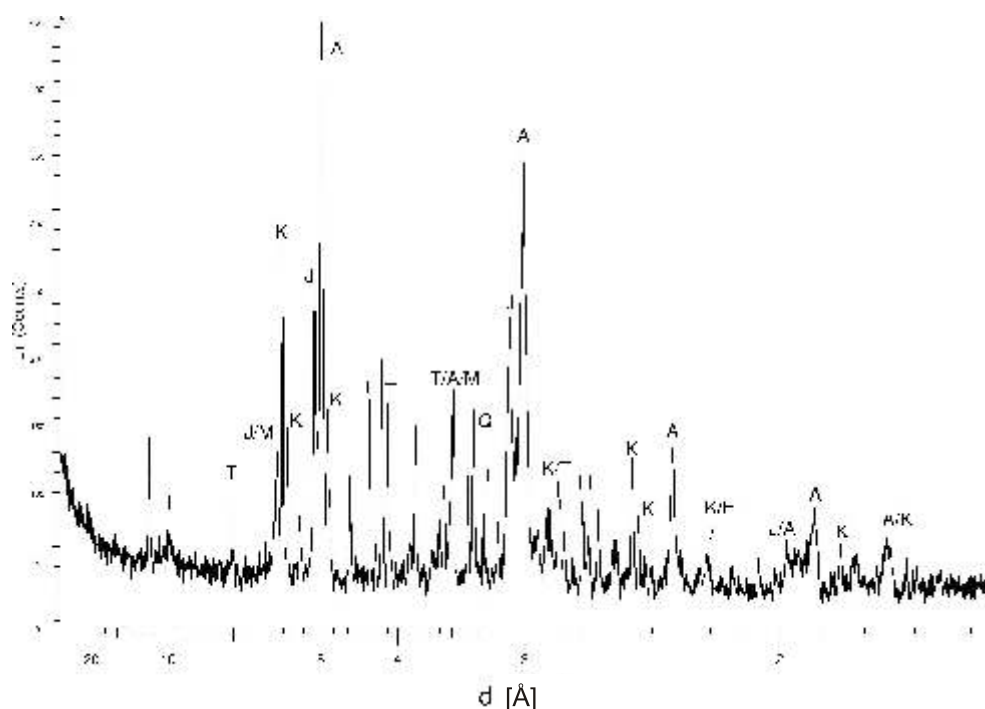
Fig. 3. Powder diffraction pattern for a kremersite-ammonioalunite assemblage

K — kremersite, A — ammonioalunite, J — ammoniojarosite, T — tschermigite,
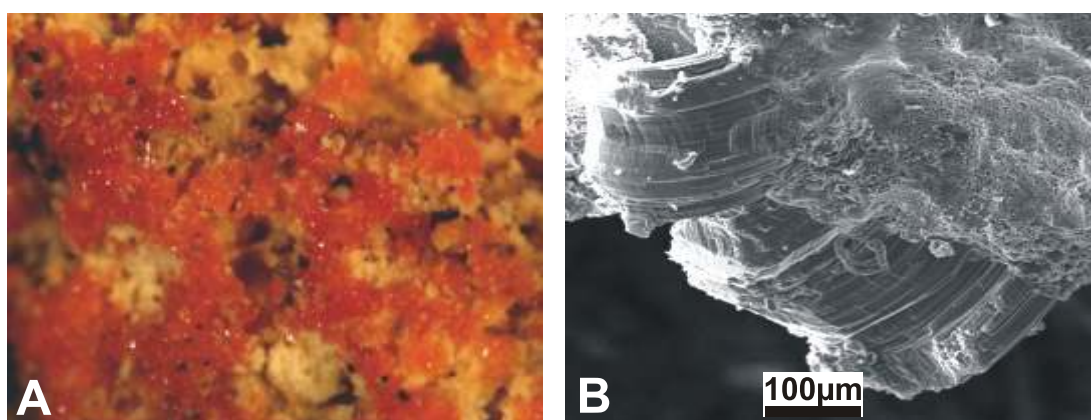M — millosevichite, H — hematite, Il — illite, Q — quartz

**Fig. 4A — orange-red kremersite aggregates on ammoniojarosite, field of view 6 mm;
B — SEM image of fibrous kremersite**

known since 1988 (type locality: the Geysers, California, USA), has been found in hot-spring environments (Altaner *et al.*, 1988). Both minerals have also been reported from some BCD (Table 1).

We identified ammoniojarosite and ammonioalunite by PXRD (Fig. 3) and EDS methods from the Czerwionka-Dębieńsko BCD in the topmost part of the sulfate crust. The composition of the crust is quite complex: godovikovite is dominant, with tschermigite, alunogen, gypsum, boussingaultite, voltaite, anhydrite, clairite, metavoltine, millosevichite, salammoniac, quartz and illite in addition. Ammonioalunite and ammoniojarosite occur as a mixture forming fine-grained porous masses, small botryoidal nodules or coatings of bright yellow to ochreous colour (Fig. 5). Ammonioalunite usually forms larger microcrystals than ammoniojarosite. They commonly have a tabular habit and are terminated by rhombohedron faces. Preliminary EDS data suggest that these minerals form here a solid solution. Compositional trends towards Na- and K-members of the alunite-jarosite series were also noticed. Crystals with alunite composition contain additional chlorine as an essential compound, probably substituting for OH. Detailed chemical data on the composition of the alunite-jarosite group from the Upper Silesian BCD will be presented elsewhere.

Fig. 5. Botryoidal aggregate of ammonioalunite-ammoniojarosite

Field of view 6 mm

TSCHERMIGITE $(NH_4)Al(SO_4)_2 \cdot 12H_2O$
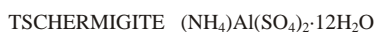
Tschermigite, named in 1853 for the type locality (Tschermig, now ermniky, Czech Republic), occurs in lignite burning seams and in volcanic solfataras and fumaroles. This natural ammonium-aluminum alum is also one of the most common NH_4-bearing sulfates on BCD (Table 1).

Tschermigite has not been recorded from Poland so far. We found this mineral at the "Skalny" dump in Łaziska, where it occurs as needles (Fig. 6A) and typically curved fibers (Fig. 6B) or botryoidal masses. Tiny imperfect crystals, locally in comb-like aggregates, were also found. At this site tschermigite, accompanied by minor gypsum, covers a hematite- and quartz-rich rock. At the Czerwionka-D bie sko BCD, tschermigite occurs in far larger amounts, both in monomineralic aggregates and as a constituent of a fine-grained mixture of minerals forming the sulfate crust (Table 3). Pure tschermigite accompanies ammoniojarosite-ammonioalunite in the topmost part of the sulfate crust. It occurs here as white, porous dendritic aggregates with a silky lustre, up to a few cm long (Fig. 6C) or small but well formed, typical octahedral crystals (Fig. 6D), infilling vugs in the crust. Tschermigite was also recognized as a constituent of a mixture of sulfate minerals with boussingaultite and clairite found far away from the sulfate crust on the same BCD. Although tschermigite is easily soluble in water, it may also be found in places where hot gas vents have not been active.
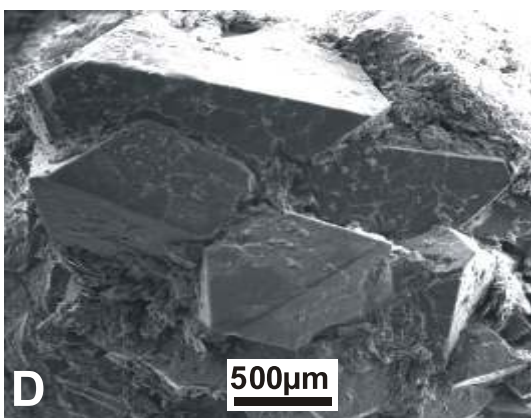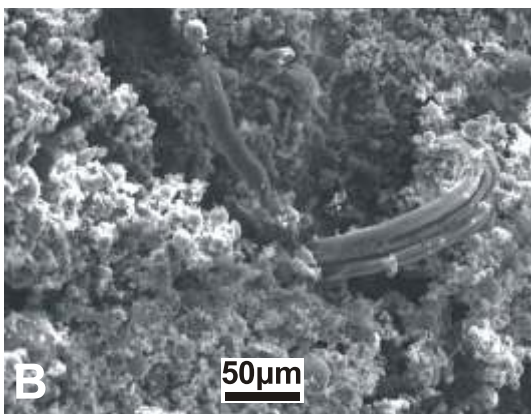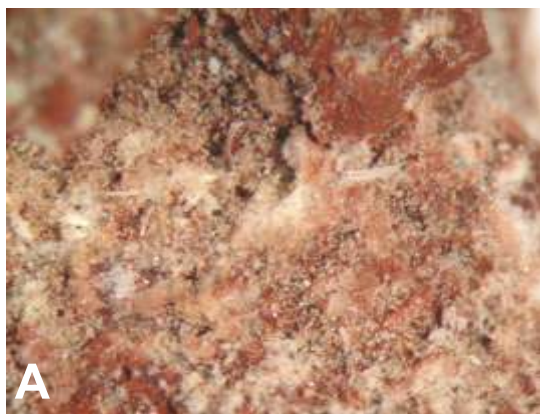
BOUSSINGAULTITE $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$

Boussingaultite, one of the natural equivalents of Tutton's salt, was first described from the geothermal fields of Travale, Tuscany, Italy, and named for the French chemist Jean-Baptiste Boussingault. Volcanic vents of the same area pro-

Fig. 6. Tschermigite crystal habits from the Upper Silesian BCD

A — tiny needles and fibers, up to 0.5 mm long on hematite, Łaziska; **B** — curved fibers, SEM image, Łaziska;
C — stalactitic-skeletal form, 1.9 cm long, Czerwionka-D bie sko; **D** — octahedral crystals, SEM image, Czerwionka-D bie sko

T a b l e 3

**X-ray powder diffraction data for tschermigite
from the Upper Silesia BCD**

| Czerwionka-D bie sko sample		PDF 07-0022		hkl
d (meas.) [Å]	(I/I₀)	d (meas.) [Å]	(I/I₀)	
7.034	22	7.070	55	111
6.102	7	6.130	12	200
5.452	18	5.480	55	210
4.98	11	4.998	35	211
4.317	69	4.327	100	220
4.068	33	4.079	80	221
3.68	15	3.691	35	311
n.o.		3.395	6	230
3.262	30	3.273	75	321
3.053	6	3.060	30	400
2.963	14	2.967	20	410
2.880	4	2.883	14	411
2.804	100	2.810	35	331
2.731	9	2.738	18	420
2.668	4	2.672	14	421
2.604	11	2.608	12	332
2.499	10	2.499	10	422
2.396	3	2.402	8	431
2.354	3	2.358	12	511
2.268	2	2.275	8	432
2.233	1	2.237	12	521
2.129	3	2.130	8	522
2.096	1	2.098	4	433
92.065	3	2.068	8	531
2.038	3	2.039	10	600
2.009	2	2.012	10	610
1.984	13	1.985	10	611
1.933	5	1.935	16	620
n.o.		1.910	2	621
1.886	2	1.888	4	541
1.865	2	1.866	8	533
1.845	1	1.846	6	622
1.823	2	1.825	6	630
1.804	1	1.805	2	631
n.o.		1.768	1	444
n.o.		1.749	2	632
1.729	1	1.731	10	543
1.713	3	1.714	4	711
1.695	2	1.698	2	640
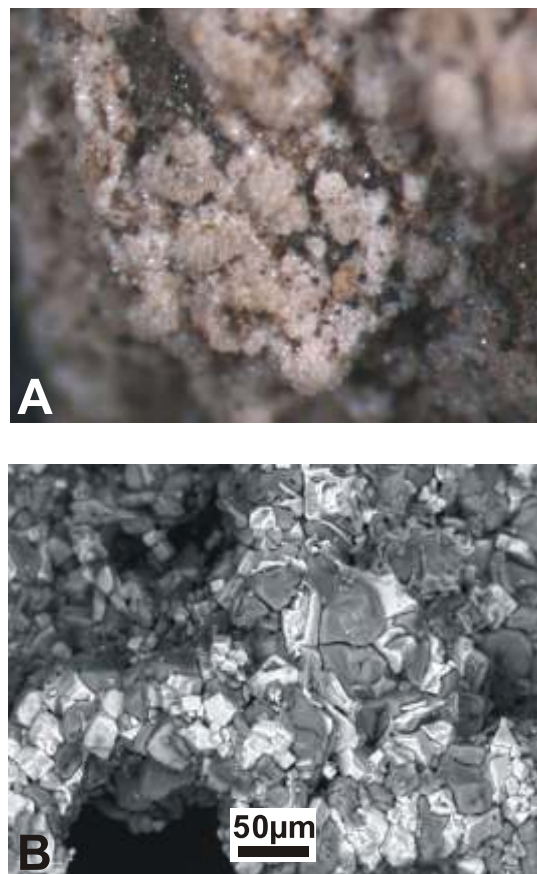
Fig. 7A — boussingaultite-halite-hexahydrite mixture, field of view 1.6 mm, Łaziska; B — SEM-BSE image of boussingaultite rounded crystals (dark) among halite cubes (light)

vide also the type locality for its Fe-analogue, mohrite (Fleischer, 1965). In general, boussingaultite is thought to be a rare sublimate of fumarolic origin. Boussingaultite occurs also on several BCD (Table 1).

In Poland boussingaultite was first found on the "Skalny" dump at Łaziska, where it occurs in small amounts as a fine-grained, porous mixture with halite and hexahydrite (Fig. 7A).

The mixture was deposited around inactive vents. Single, short prismatic, often rounded boussingaultite crystals reach 50 μm in width (Fig. 7B). SEM-EDS analyses show that some of them contain essential K, suggesting a composition within the boussingaultite-picromerite solid solution series.

Boussingaultite was also detected as one of the main constituents of an assemblage with tschermigite, clairite, and ammonioalunite-ammoniojarosite (Fig. 8) at the Czerwionka-D bie sko BCD. Small admixtures of this mineral were also recognized among minerals forming the uppermost part of the sulfate crust at the Czerwionka-D bie sko BCD. Boussingaultite, an easily soluble mineral, can persist only in favorable weather conditions on the BCD surface.

CLAIRITE $(NH_4)_2Fe_3(SO_4)_4(OH)_3 \cdot 3H_2O$

Clairite was originally described by Martini in 1983 from Lone Creek Fall Cave near Sabie, Eastern Transvaal, RSA, and
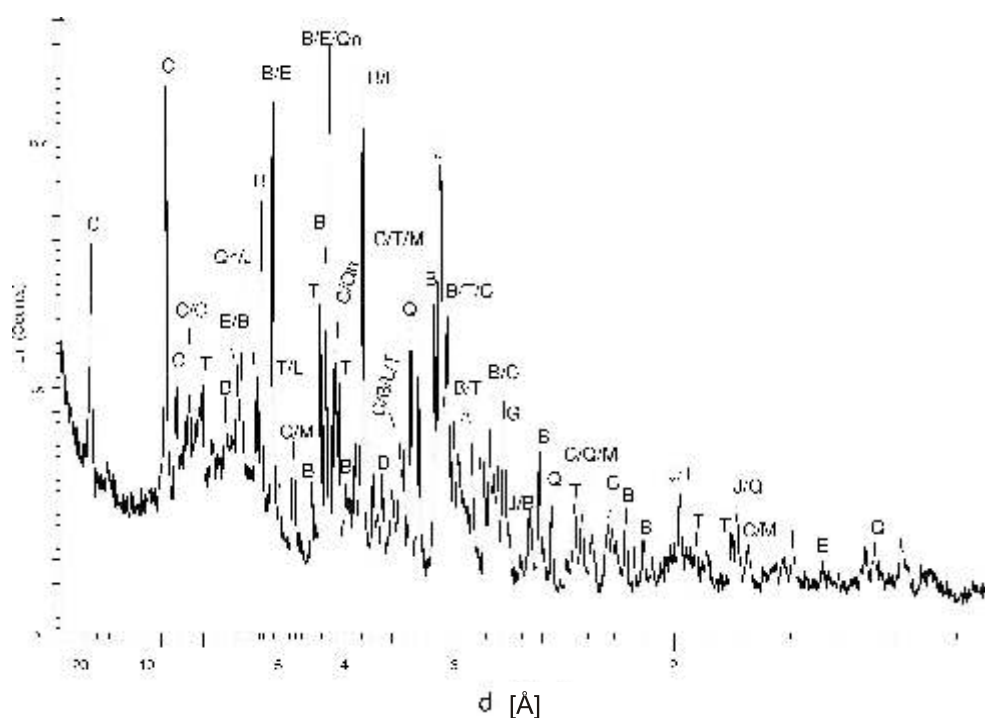
Fig. 8. Powder diffraction pattern for clairite-boussingaultite assemblage

B — boussingaultite, C — clairite, E — epsomite, G — gypsum, J — ammoniojarosite, L — letovicite,
M — metavoltine, T — tschermigite, Q — quartz, Qn — quenstedtite

named for his wife (Dunn *et al*., 1986). At the type locality, clairite, and associated lonecreekite and sabieite, are formed by the reaction of pyrite oxidation products with NH_3 from the decay of organic matter. To our best knowledge, this mineral has been reported from only one BCD locality (Table 1), although it is probably more common in this environment.

Here we report the first Polish occurrence of clairite. It was found with boussingaultite among non-burnt black shale fragments richly impregnated with salammoniac, accompanied by minor tschermigite, rostite, mascagnite and ammonioalunite-ammoniojarosite, on the Czerwionka-Dębieńsko BCD (Fig. 8). Clairite and boussingaultite are essential constituents of brownish-yellow, fine grained clots or powdery masses (Fig. 9A). They are very difficult to distinguish macroscopically from yel-

low cryptocrystalline metavoltine intimately intergrown with hexahydrite, occurring at the same site. Clairite forms minute triclinic blades, up to about 10 µm wide, with pseudohexagonal outlines, somewhat resembling those of the alunite-jarosite group. Clairite crystals are often grouped into rosette clusters and grow on or close to euhedral crystals of boussingaultite (Fig. 9B). Clairite was also found as a very minor constituent of the cover sulfate crust developed on the same BCD, where it is closely associated with tschermigite, voltaite and metavoltine.

EFREMOVITE $(NH_4)_2Mg_2(SO_4)_3$

This anhydrous ammonium magnesium sulfate, named for the Russian geologist I. A. Yefremov, was first described by
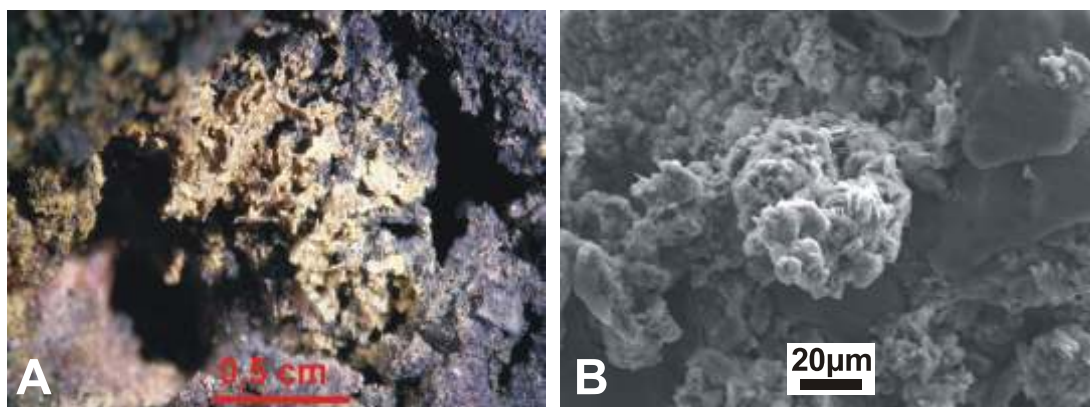

Fig. 9A — clairite-bearing assemblage from Czerwionka-Dębieńsko; B — clairite rosette by rounded boussingaultite, SEM image
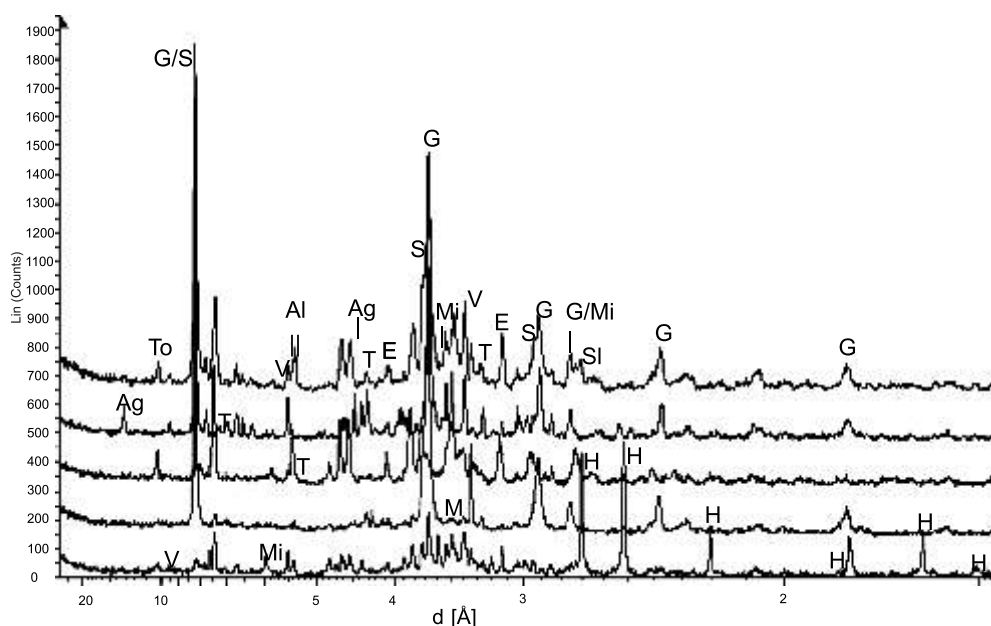
Fig. 10. Powder diffraction patterns for godovikovite-bearing assemblages

Ag — alunogen, Al — ammonioleucite, E — efremovite, G — godovikovite, H — hematite, M — millosevichite,
Mi — mikasaite, S — sabieite, Sl — salammoniac, To — tobelite (or NH_4-bearing muscovite), V — voltaite

Shcherbakova and Bazhenova in 1989 from BCD of the Chelyabinsk Coal Basin, Southern Urals, Russia (Jambor and Grew, 1991). The type material forms white to gray aggregates of equant grains ranging from 0.01–0.015 mm. The authors suggested a pseudofumarolic origin for the mineral. The sulfate crust of the type locality comprises (from top to bottom): unconsolidated material, an asphalt-like organic substance encrusted with native sulfur and kladnoite, crustal to stalactitic mascagnite and dense white masses of mainly efremovite, which in their upper part is hydrated to boussingaultite. Efremovite is thought to be formed by the decomposition of dolomitic rocks by H_2SO_4 and coal-derived NH_3 in the temperature range of 180–400°C. Godovikovite-associated organic matter presumably here inhibits the hydration of efremovite. Under normal conditions, it takes only several days for efremovite to be completely hydrated to boussingaultite.

For the first time in Poland, we detected small amounts of efremovite by PXRD, in association with godovikovite in the sulfate crust of the Czerwionka-Dębieńsko BCD (Fig. 10). Some boussingaultite on the Upper Silesian BCD may be a hydration product of efremovite.

GODOVIKOVITE $(NH_4)(Al,Fe)(SO_4)_2$
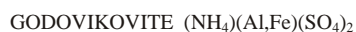
Godovikovite, named for the Russian mineralogist A. A. Godovikov, was introduced by Shcherbakova, Bazhenova and Chesnokov in 1988 (Jambor and Grew, 1990). At the type locality, which are BCD near Kopeysk (Chelyabinsk Coal Basin, Southern Ural Mts., Russia), it occurs as white, chalky, compact to porous aggregates, composed of 0.001 to 0.015 mm

long hair-like crystals. Godovikovite from the Russian locality is described as primary and a major constituent of sulfate crusts, that are formed by reaction of gases generated by coal fires with the dump waste-rocks. Godovikovite occurs in the inner, hotter zone of the sulfate crust, which is up to 5 cm thick and extends up to 1 m^2. This mineral was later found at several other BCD worldwide (Table 1).

We found godovikovite, previously unknown in Poland, as very abundant, white to gray masses, building up a thick sulfate crust formed at the Czerwionka-Dębieńsko BCD. Table 4 presents powder X-ray diffraction data for this material. Due to movement of the pile material the sulfate crust becomes accessible on the surface. The crust temperature reaches a maximum of 100°C, when measured a few cm below the surface. The godovikovite masses have a very typical vesicular texture (Fig. 11A), mentioned i.e. by Stracher *et al.* (2005). Godovikovite can form stalactites often with nodosity (Fig. 11B), which attain a few cm in length. SEM images show that godovikovite masses are composed of chaotically arranged, tabular micro-blades with hexagonal outlines, usually about 5 µm across (Fig. 11C). Some crystals of godovikovite have a skeletal framework, suggesting rapid crystallization. EDS analyses of godovikovite blades show, as a rule, small admixtures of Fe. Some godovikovite aggregates also contain essential Si. This is consistent with PXRD data, which shows the possible presence of an admixture of ammonioleucite and tobelite (a NH_4-analogue of muscovite). The results of PXRD indicated that godovikovite is also accompanied by subordinate alunogen, tschermigite, ferrinatrite and starkeyite (Fig. 10). Tiny yellowish crusts on godovikovite masses contain some
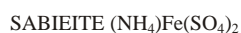
T a b l e　4

X-ray powder diffraction data for godovikovite from Czerwionka-Dębieńsko BCD

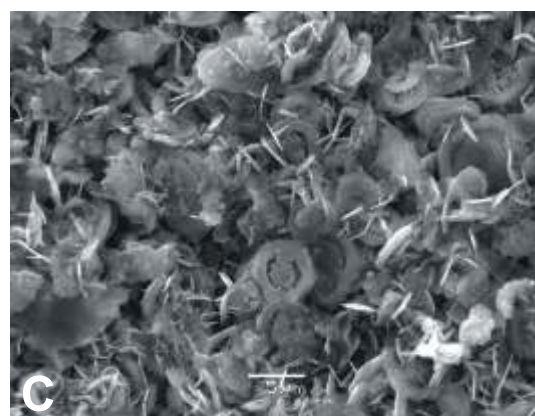| Czerwionka-Dębieńsko sample		PDF 23-0001		hkl
d (meas.) [Å]	(I/I_o)	d (meas.) [Å]	(I/I_o)	
8.143	100	8.280	60	001
4.073	4	4.140	1	002
3.660	67	3.678	100	101
2.908	21	2.915	30	102
2.747	9	2.759	9	003
2.370	11	2.368	15	110
2.292	3	2.291	2	103
2.276	4	2.277	3	111
2.070	4	2.071	2	004
2.057	5	2.056	3	112
2.051	3	2.051	2	200
1.989	3	1.991	3	201
1.847	5	1.849	7	104
1.840	6	1.839	8	202
1.801	2	1.798	1	113
1.656	2	1.656	1	005
1.646	2	1.647	3	203
1.559	3	1.559	2	114
1.552	2	1.550	1	210
1.536	3	1.536	2	105
1.526	4	1.525	7	211
1.459	3	1.457	4	204
1.452	2	1.453	5	212
1.380	1	1.381	1	006
1.366	4	1.367	6	300
1.356	4	1.357	5	115
1.350	2	1.349	2	301

Fig. 11A — vesicular mass of stalactitic-like godovikovite, field of view 1.4 cm; B — nodosity in a godovikovite stalactite, field of view 2.4 cm; C — pseudohexagonal blades of godovikovite, SEM image

copiapite, voltaite, metavoltine and ammonioalunite-ammoniojarosite. On the godovikovite surface black spheres up to *ca.* 2 mm wide, composed of hematite, voltaite, mikasaite, millosevichite, kieserite, ammonioleucite and tobelite, were also found.

Godovikovite is a slightly hygroscopic mineral. Storage under room conditions for a few months does not cause its hydration or any other change.

SABIEITE (NH₄)Fe(SO₄)₂

Sabieite, the Fe analogue of godovikovite, was found together with clairite and lonecreekite at Lone Creek Cave near Sabie, Transvaal (Dunn *et al*., 1986) and named for the locality.

This very rare mineral was also reported from a BCD at the Lichtenberg Absetzer mine dump in Germany (Witzke and Rüger, 1998). Our find of sabieite at Czerwionka-Dębieńsko is probably the second occurrence of this mineral on a BCD and the first in Poland. We detected sabieite by the PXRD method as an admixture in godovikovite (Fig. 10). Sabieite was an essential compound of some parts of the godovikovite aggregates, especially those of gray colour.

The holotype sabieite is thought to be formed by dehydration of lonecreekite (Fe-analogue of tschermigite), whilst the BCD sabieite is probably of pseudofumarolic origin, as is the case of godovikovite.
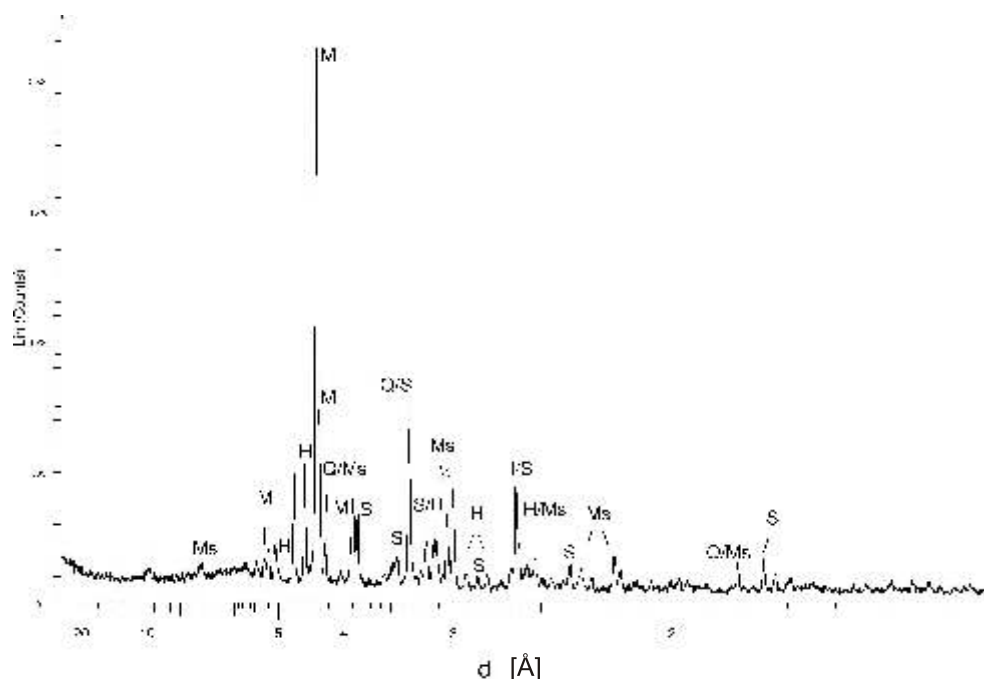
Fig. 12. Powder diffraction patern for a mascagnite-bearing assemblage

I — illite, H — hexahydrite, M — mascagnite, Ms — millosevichite, Q — quartz, S — native sulfur

MASCAGNITE $(NH_4)_2SO_4$

The natural anhydrous ammonium sulfate, named in 1779 for Paolo Mascagni, who first described the mineral, is produced by sublimation among fumaroles and solfataras. Mascagnite is commonly known also from BCD (see Table 1). We detected this mineral, until now unknown from Poland, on a small BCD in Zabrze-Biskupice. Mascagnite was associated with native sulfur and minor millosevichite (Fig. 12). On SEM images (Fig. 13) this mineral forms aggregates of randomly arranged, minute needle-like crystals growing on sulfur efflorescences. The genetic relationship of these two minerals as sublimates 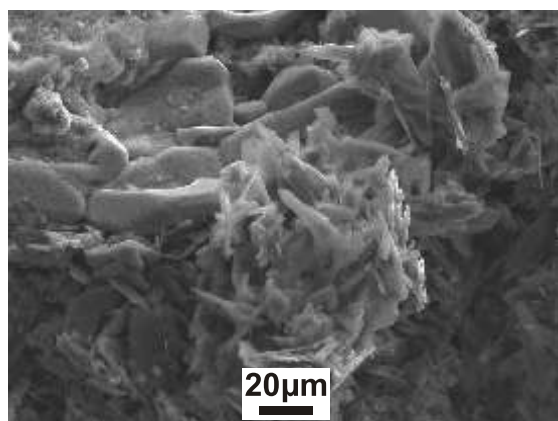is typical of BCD environments. Small amounts of mascagnite were also found with salammoniac at the Czerwionka-D bie sko BCD. At the same dump mascagnite occurs as a subordinate compound in the cover of the sulfate crust, where it is closely associated with godovikovite, tschermigite and salammoniac.

FORMATION OF AMMONIUM MINERALS ON BCD

The ammonium minerals occurring on BCD can be divided into two groups, depending on the source of the elements required (Stracher *et al.*, 2005). One group comprises salammoniac, native sulfur and mascagnite which could be formed by simple coal-derived gas condensation, as these minerals contain elements typically concentrated in the organic compounds of coal. Formation of other NH_4- minerals requires a source of metallic compounds extracted from the waste rocks of the BCD. Magnesium (and calcium) are likely derived from carbonate minerals: dolomite, ankerite, iron from pyrite and siderite, and aluminum from clay minerals or feldspars. These minerals are unstable in the hot, central part of the fire zone and undergo thermal decomposition or are attacked by aggressive fire gases. Hot fluids rich in sulfuric acid, forming the sulfate crust near the fire zone, are of special importance here. Most sulfur and chlorine compounds of the sulfate assemblages can also be derived from minerals present in the coal seams, pyrite and halite, respectively. We suspect the ammonia originated from the thermal decomposition of coal macerals or alternatively by its synthesis from air nitrogen in the hottest fire.

Fig. 13. Mascagnite needles on native sulfur, SEM image, Zabrze-Biskupice

Essential information on mineral genesis can be discerned from the habit of the mineral aggregates and crystals. The observed vesicular texture of some sulfates, i.e. godovikovite, is explained as a mark of the escape of a vapor, released during crystallization. Formation of the sulfate crust at the Czerwionka-Dębieńsko BCD took place under labile temperature conditions related to the fire-centre distance.

A fibrous or dendritic habit of tschermigite and salammoniac resulted from rapid gas condensation, as such conditions would favor the appearance of ill-defined forms rather than well-developed crystals. This habit is typical of mineral assemblages occurring around gas vents on the surface. Larger, clearly euhedral crystals represent slow condensation and are usually found somewhat deeper.

Except for the ammoniojarosite-ammonioalunite series, all the ammonium minerals detected are water-soluble, thus their crystallization and preservation depend on environment humidity. Even minerals thought to be formed by gas condensation, such as tschermigite and salammoniac, may precipitate from locally formed aqueous solutions by cooling or evaporation. Presumably isometric crystals of both minerals are products of recrystallization. In the outer part of the sulfate crust, hydration of primarily anhydrous sulfates contributed to the development of the currently observed assemblage. One such possible change is given as the reaction:

$$(NH_4)Al(SO_4)_2 + 12H_2O \rightarrow (NH_4)Al(SO_4)_2 \cdot 12H_2O$$
$$\text{godovikovite} \qquad\qquad\qquad \text{tschermigite}$$
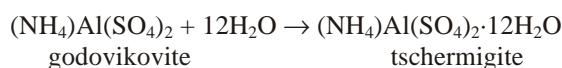
A similar transformation was reported from the Ravat coal fire site by Nasdala and Pekov (1993) for an anhydrous Al sulfate (likely millosevichite), where alunogen is the product of its hydration. The hydration of godovikovite or of other anhydrous sulfates may be reversible, depending on temperature. Hydrated sulfate minerals reported from the supergene zone of BCD, as a rule, are formed due to their mutual transformation (dissolution and next crystallization), similarly to processes known from K-Mg salt deposits and the weathering zones of sulfides and acid mine drainage.

Besides being of scientific interest, efflorescences of ammonium minerals on the surface of coal waste piles may be recognized as useful indicators of underground fires.

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