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ON THE OCCURRENCE OF ASCHARITE IN THE KŁODAWA SALT DOME

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Abstract. Ascharite $Mg_2[B_2O_4OH]OH$ was found in the Zechstein salt deposit of the Kłodawa region within the horizon of the younger potassium salts (Z_3). It occurs as massive fine-grained aggregates embedded in kieserite-bearing carnallite rock. The mineral was identified using optical and electron microscopy, X-ray and infrared absorption analysis. Ascharite is the second borate mineral identified in this deposit, besides of boracite, reported earlier by Prochazka (1957) and Hanczke (1969).

Ascharite was found by the present writer within the Kłodawa salt mine, in the horizon of the younger potassium salts (Z_3), 600 metres below the surface in the galleries NE III and NE-SW X. These galleries cut nearly vertically dipping carnallite rocks with banded structure. It is second borate mineral identified in the Zechstein salt deposit of the Kujawy region since the occurrence of boracite in Inowrocław was reported by Prochazka (1957) and in Kłodawa by Hanczke (1969). The ascharite-bearing rock consists mainly of carnallite with lesser amounts of halite, kieserite, anhydrite, kainite and traces of boracite. Carnallite forms light grey, pink or red anhedral grains, showing sometimes polysynthetic twinning. Its banded colouration is caused by cyclic alteration of the quantity of haematite flakes admixture. Fine-grained kieserite associated with small amount of euhedral anhydrite occurs as periodically distributed, white-greyish accumulations. This together with changing colouration of carnallite gived the effect of banding characteristic of the rock in question. The kainite grains are anhedral, yellowish in colour, often displaying twin structures (Charysz & Fijał, in press). Boracite forms fine kidney-shaped aggregates within the carnallite rock. Ascharite occurs as fine-grained aggregates embedded among kieserite grains and only rarely within carnallite groundmass (Pl. I photos. 1 and 2).

Ascharite has monoclinic symmetry (space group C^5_{2h} — P2/c; $Z = 4$).

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The essential element of its structure are double-condensed flat BO_3^{3-} anions, with one of oxygens substituted by OH group. Mg atoms occur in octahedral coordination as $Mg(O,OH)_6$ groups. These octahedra are linked by common edges forming columns extending along C axis (after Povarennykh 1966).

Identification of the mineral in question was carried out basing on the results of microscope, X-ray and infra-red spectrophotometric examinations. Ascharite was separated from the rock on the ground of its very low solubility in water when compared with other salt minerals associated with it.

Ascharite forms colourless crystals displaying vitreous lustre. Its average refractive index is ca 1.608, being charakteristic of the ascharite variety occurring in massive fine-grained aggregates (Yarzhemskii 1966).

Determination of grain-size of this mineral, as well as of the shape and morphology of its crystals was possible only by means of electron microscopy. As follows from the photographs thus obtained (Pl. II photos. 3 and 4) ascharite crystals are prismatic or needle-shaped and their size varies between 0.001 and 0.01 mm. Basing on the electron diffraction pattern of this mineral (Pl. III phot. 5) d_{hkl} values were calculated, confirming the identity of this mineral.

X-ray powder pattern was obtained using filtered CuK$_\alpha$-radiation in cameras 114.6 mm in diameter. As follows from the data presented in Table 1 they are fairly concordant with those of standard ascharite (Brovkin et Nekrasov 1966).

Infra-red absorption analysis was carried out with Zeiss's UR-10 spectrophotometer applying KBr discs technique. The spectrum (Fig. 1) was registered within the wave number ranges 400—1800 and 2800—3800 cm^{-1}. It is very similar to the standard one after Moenke (1962). The essential absorption bands of this spectrum are connected with various vibrations within condensed (B_2O_4OH) anions and $Mg(O,OH)_6$ octahedra. The number and position of absorption bands indicate the occurrence of two crystallochemically non-equivalent B^{3+} cations in the complex anion. Taking into account the model of structure of this polyanion its symmetry is assumed to be C_1. This causes their activity in infra-red. 18 normal vibration modes should be distinguished for such type of polyanion, 12 of which would be connected with internal vibrations of (B_2O_4OH) group. When compared with vibrations of (BO_3) ion there occur a double amount of vibrations of ν_1, ν_2, ν_3 and ν_4 type. The region of symmetric stretching ν_1 lies approximately at 950 cm^{-1}, that of out-of-plane bending ν_2 — approximately at 750 cm^{-1}. Moreover the wave number range of ca. 1250 cm^{-1} correspond to ν_3 vibrations (antisymmetric stretching) whereas that of ca. 600 cm^{-1} to ν_4 ones (in-plane bending). Subsequent three vibration modes are connected with three translation vibrations of one triangular BO_3 group relative to the other one. Their vibration frequencies are situated most probably in the range of low wave numbers, outside of registration range of the apparatus because of large mass of vibrating atom groups. Finally there occur vibrations within the OH-groups of polyanions. These are ν-OH, δ-OH and γ-OH vibrations. The presence of bands corresponding to these vibrations and lack of the absorption maximum at ca. 1650 cm^{-1} connected with δ-H_2O vibrations definitely confirm the absence of water molecules in the crystal lattice of ascharite. Sharp, intense band corresponding to valence vibrations of hydroxyl groups at 3570 cm^{-1} suggests rather poor participation of OH groups in hydrogen bonds. Interpretation of infra-red absorption spectra is made a little more difficult due to the presence of two boron isotopes (B^{10} — 18.98% and B^{11} — 81.02%), causing characteristic band displacement connected with various frequencies of B^{11}-O and B^{10}-O vibrations, the valence vibrations of heavier systems corresponding to lower wave numbers. Consequently the obtained spectrum contains an increased amount of absorption bands. A precise determination of positions of B^{10}-O and B^{11}-O maxima would be possible if synthetic ascharite varieties containing only boron isotope in complex anion were examined.

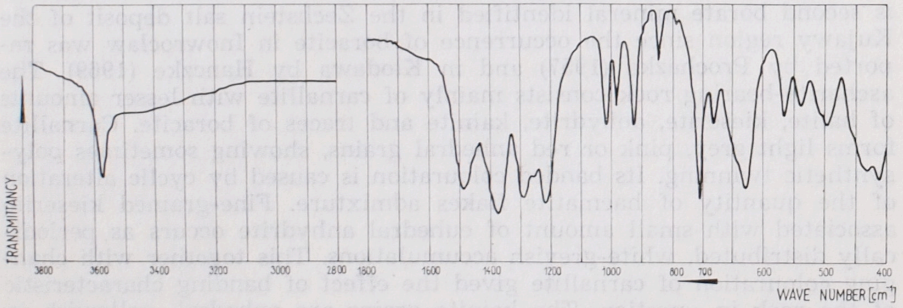

Fig. 1. Infra-red absorption spectrum of ascharite from Kłodawa

It should be emphasized that infra-red absorption spectrophotometry is very useful in the phase analysis of salt rocks. The presence of borate minerals in specimens of kieserite-bearing carnallite rock was revealed just basing on infra-red absorption spectra. In examining the rocks in question this method displays higher sensitivity than X-ray analysis.

Because of low concentration of boron in sea water, precipitation of its compounds is possible only in the last stage of crystallization of evaporites i.e. simultaneously with potassium-magnesium salts. The formation of separate boron minerals is connected with its specific crystallochemical properties determining its behaviour in nature and its geochemical position. They are governed first of all by small size and large charge of boron ions and by high ionization potential of this element. Consequently boron does not form ionic compounds and does not occur as cation in nature, forming complex anions with strong covalent bonds. Generally boron is coordinated with oxygen and its simplest coordination grouping is the anion BO_3^{3-}. The latter shows specific tendency to polymerize. Thus, in nature there occur various types of condensed polyhedral anions, being characteristic of hypergenic borates. In magmatic rocks this element generally occurs in tetrahedral BO_4^{5-} groups, being able to replace SiO_4^{4-} anions. The structure of borates resulting from polymeri-

Table 1

X-ray powder data for ascharite

from Kłodawa (Poland)		according to Brovkin and Nekrasov (1966)	
I	*d* (Å)	*I*	*d* (Å)
10	6.25	9	6.25
2	5.19	2	5.22
2	3.80	1	3.88
2	3.396	3	3.349
5	3.254	5	3.260
4	3.034	5	3.033
5	2.987	6	2.986
2	2.807	4	2.807
10	2.664	10	2.669
3	2.597	3	2.596
5	2.557	5	2.564
6	2.542	8	2.543
10	2.434	10	2.432
2	2.381	1	2.383
7	2.316	8	2.316
10	2.206	10	2.205
9	2.084	9	2.082
—	—	<1	2.054
2	2.032	1	2.026
5	1.998	8	1.995
1	1.976	1	1.976
2	1.937	2	1.939
—	—	1	1.909
1	1.868	1	1.868
3	1.794	5	1.794
3	1.762	1	1.759
5	1.731	7	1.728
3	1.692	3	1.691

zation processes depends on concentration of BO_3^{3-} anions, nature of compounds containing boron, temperature of the system and quality of cations in the crystallizing solution. Consequently there is a considerable variety of borate minerals occurring in sedimentary salt rocks. Later hydration and diagenetic processes developing in salt deposits are responsible for further increase of the number of boron minerals. These alterations generally tend to replace less stable structures by more stable ones as e.g. that of ascharite. Secondary origin of this mineral in the rocks under consideration is evidenced by its mode of occurrence. Similarly as coexisting boracite it forms very fine-grained aggregates among kieserite grains. Such aggregates are formed either during replacement of less stable borates by ascharite or result from the action of boron-rich saline waters on kieserite.

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Jerzy FIJAŁ

O WYSTĘPOWANIU ASCHARYTU W KŁODAWSKIM WYSADZIE SOLNYM

Streszczenie

Obecność ascharytu $Mg_2[B_2O_4OH]OH$ stwierdzono na terenie złoża soli w Kłodawie wśród młodszej soli potasowej Z_3, w karnalitowcu kizerytowym (na poziomie 600 m w chodnikach NE 3 i NE-SW 10). Chodniki te przebijają zapadające niemal pionowo w tych partiach złoża utwory solne, ujawniając teksturę warstwowaną skały karnalitowej. Jest ona wywołana pasmowym ułożeniem białoszarawych skupień drobnoziarnistego kizerytu z domieszką niewielkich ilości anhydrytu, jak również cyklicznie powtarzającym się czerwonym zabarwieniem karnalitu pochodzącym od domieszki drobnych blaszek hematytowych. Ascharyt tworzy drobnoziarniste jasnoszare skupienia, głównie wśród ziarn kizerytu, rzadziej karnalitu (Pl. I, fot. 1 i 2).

Identyfikacji ascharytu dokonano na podstawie badań mikroskopowych, rentgenograficznych i spektrofotometrycznych w podczerwieni. Do badań tych wydzielono minerał ze skały, wykorzystując jego bardzo małą rozpuszczalność w wodzie. Średni współczynnik załamania światła ascharytu z Kłodawy wynosi około 1,608. Jego odległości międzypłaszczyznowe przedstawiono w tabeli 1 obok danych porównawczych według Browkina i Niekrasowa (1966), a widmo absorpcyjne w podczerwieni na figurze 1.

Określenie wielkości kryształów badanego minerału i ich pokroju stało się możliwe dzięki zastosowaniu mikroskopu elektronowego. Uzys-

kane tą metodą zdjęcia (Pl. II, fot. 3 i 4) obrazują słupkowaty, igiełkowaty pokrój kryształów ascharytu o wielkości 0,001—0,01 mm. Na podstawie obrazu dyfrakcji elektronowej na kryształach tego minerału (fot. 5) obliczono kilka wartości d_{hkl}, które potwierdzają trafność jego identyfikacji.

Ascharyt jest drugim minerałem boranowym stwierdzonym w kujawskich złożach solnych, obok boracytu opisanego przez Prochazkę (1957) i Hanczke (1969). Jest to zapewne minerał wtórny, o czym świadczy m.in. jego forma występowania w skale.

OBJAŚNIENIE FIGURY

Fig. 1. Widmo absorpcyjne w podczerwieni ascharytu z Kłodawy

Ежи ФИЯЛ

О РАСПРОСТРАНЕНИИ АШАРИТА В КЛОДАВСКОМ СОЛЯНОМ КУПОЛЕ

Резюме

Ашарит $Mg_2[B_2O_4OH]OH$ был определен в месторождении соли в Клодаве среди младшей калийной соли Z_3, в кизеритовом карналлитолите (горизонт 600 м, штреки СВ 3 и СВ-ЮЗ 10). Соляная залежь, характеризующаяся слоистой текстурой карналлитовой породы, залегает здесь почти вертикально. Слоистость вызвана полосчатым чередованием беловато-серых скоплений мелкозернистого кизерита с примесью небольшого количества ангидрита и циклическим появлением красноватого карналлита, окрашенного примесью мелких чешуек гематита. Ашарит образует мелкозернистые светлосерые скопления, распространенные главным образом в кизерите, реже в карналлите (Табл. 1, фото 1 и 2).

Определение ашарита производилось микроскопическим, рентгенографическим и инфракрасным спектральным методами. Этот минерал был извлечен из породы с использованием его слабой растворимости в воде. Средний коэффициент преломления света ашарита из Клодавы составляет около 1.608. Его межплоскостные расстояния, вместе со сравнительными данными Бровкина и Некрасова (1966), представлены в таблице 1, спектр полощения — на фигуре 1.

Возможность определения величины и формы кристаллов исследованного минерала появилась благодаря применению электронного микроскопа. Полученные таким методом снимки (Табл. II, фото 3 и 4) показывают шестоватую, игольчатую форму кристаллов ашарита величиной 0.001—0.01 мм. На основании вида электронной диффракции на кристаллах этого минерала (Табл. III, фото 5) определено несколько величин d_{hkl}, которые подтверждают его правильное определение.

Аширит является вторым боратом, выявленным в соляных копях Куявии, после борацита, описанного Прохазкой (1957) и Ханчке (1969). Он представляет, вероятно, вторичный минерал, о чем говорит его форма распространения в породе.

ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. Спектр поглощения ашарита из Клодавы

PLATE I (PLANSZA I, ТАБЛИЦА I)

Phot. 1. Fine-grained ascharite aggregations in carnallite-kieserite rock. Crossed nicols, magn. 120×
a — ascharite (grey), *h* — halite (dark), *k* — carnallite, *ki* — kieserite

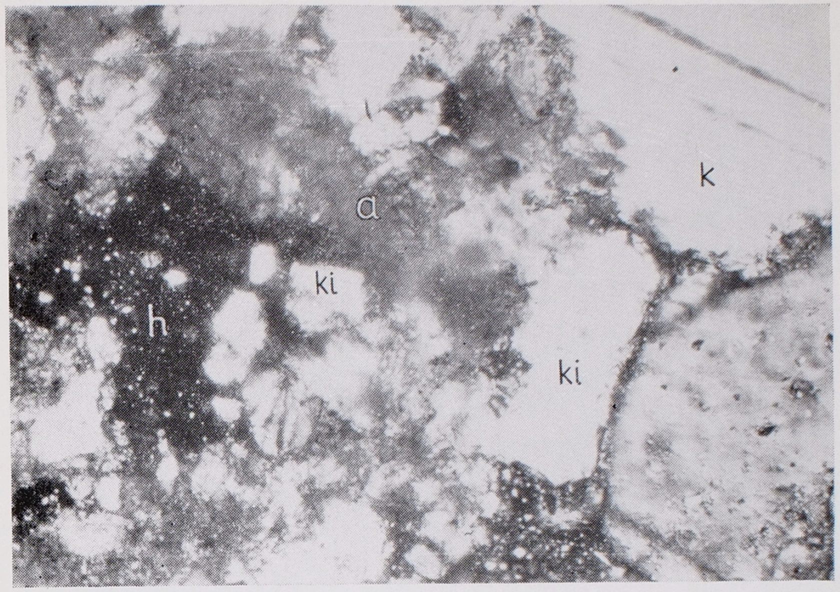
Drobnoziarniste skupienia ascharytu w karnalitowcu kizerytowym. Nikole skrzyżowane, pow. 120×
a — ascharyt (szary), *h* — halit (ciemny), *k* — karnalit, *ki* — kizeryt

Мелкозернистые скопления ашарита в кизеритовом карналлитолите. Николи X, увел. 120×
a — ашарит (серый), *h* — галит (темный), *k* — карналлит, *ki* — кизерит,

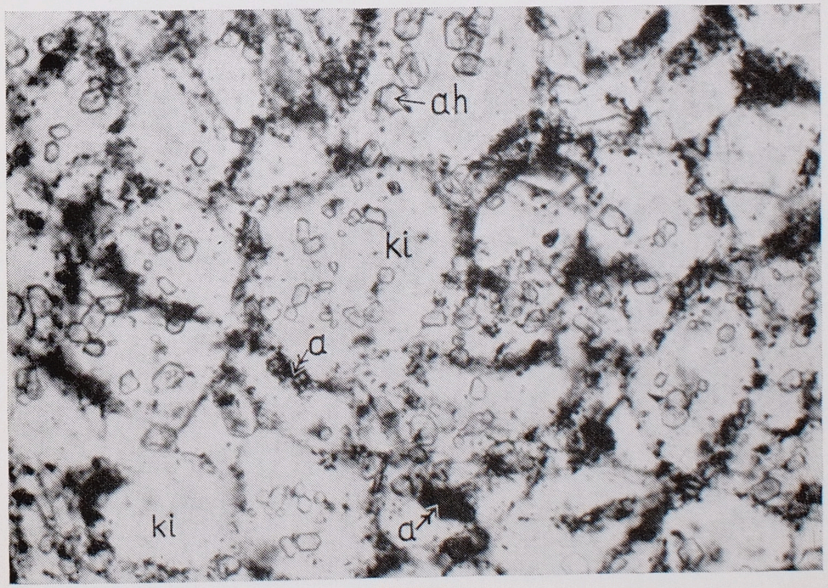
Phot. 2. Ascharite aggregations between kieserite grains. Plane polarized light, magn. 120×
a — ascharite (grey), *ki* — kieserite, *ah* — anhydrite

Skupienia ascharytu między ziarnami kizerytu. 1 nikol, pow. 120×
a — ascharyt (szary), *ki* — kizeryt, *ah* — anhydryt

Скопления ашарита между зернами кизерита. I николь, увел. 120×
a — ашарит (серый), *ki* — кизерит, *ah* — ангидрит



Phot. 1



Phot. 2

Jerzy FIJAŁ — On the occurrence of ascharite in the Kłodawa salt dome

PLATE II (PLANSZA II, ТАБЛИЦА II)

Phot. 3. Electron micrograph of ascharite crystals. Magn. ca. 9000×
Elektronowy obraz kryształów ascharytu. Pow. ok. 9000×
Електронное изображение кристаллов ашарита. Увел. ок. 9000×

Phot. 4. Electron micrograph of ascharite crystals. Magn. ca. 14 000×
Elektronowy obraz kryształów ascharytu. Pow. ok. 14 000×
Електронное изображение кристаллов ашарита. Увел. ок. 14 000×

Phot. 3

Phot. 4

Jerzy FIJAŁ — On the occurrence of ascharite in the Kłodawa salt dome

PLATE III (PLANSZA III, ТАБЛИЦА III)

Phot. 5. Electron diffraction photograph of ascharite
Obraz dyfrakcji elektronowej na krysztale ascharytu
Вид електронной дифракции на кристалле ашарита

Phot. 5