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BASALUMINITE IN THE WEATHERING ZONE OF CARPATHIAN FLYSCH DEPOSITS

UKD 549.766.423.01/02.08:551.781.3/4:551.311.23(438.31-12-924.51)

Abstract. A powdery or compact, white to faintly yellowish brown sulphate mineral forming coatings and crack or joint infillings was found in abundance in Hieroglyphic beds, one of Flysch formations of the Northern Carpathians. Originated by interaction of sulphuric acid produced by pyrite decomposition with kaolinite-rich sediments, this supergene mineral can be observed on dry slopes of the outcropping shales with sandstone and mudstone lenses or interlayers. The last mentioned permeable sediments are responsible for the seasonal strata- or valley-sources outpouring near the water-level of the artificial Rożnów dam-lake. The list of accompanying minerals embraces gibbsite, allophane, gypsum, hydrated Fe and Mn oxides and in farther neighbourhood — jarosite (in shales only). Basaluminite is the most stable, less hydrated form of hydrobasaluminite, precipitation product of dilute Al- and SO₄-rich and SiO₂-poor solutions or a replacement product of earlier formed allophane and gibbsite. Gibbsite is also the final, stable link in the hydrolysis processes of Al-sulphates.

INTRODUCTION

In the mineral world there are many examples of abundance underestimation. Basaluminite presents such a case. Known from only a few occurrences in England, France, USSR and USA it is surely a much more common mineral. The chief agents and environmental conditions are included in the oxidation and hydration of pyrite in mildly wet climate conditions to sulphuric acid and in the interaction of this acid with the country rock, especially if composed of relatively Al-rich and acid-soluble minerals, such as kaolinite. Kaolinite and pyrite as the source minerals for supergene hydrobasaluminite and basaluminite were reported in nearly all cases: 1-o by Hollingworth and Bannister (1950) — in siderite-chamosite mudstones (Inferior Oolite, Jurassic) with allophane, halloysite, aragonite, gypsum and Fe and Mn oxides, 2-o by Pei-Lin Tien (1968) — in shales of Cabannis formation (Middle Pennsylvanian) with gypsum, allophane and iron oxides, 3-o by Sunderman and Beck (1969) —

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in residual clays of early Pennsylvanian age with halloysite, allophane, gibbsite and hydrated Fe and Mn oxides, 4-o by Fominyh (1965) — in secondary quartzites of pyrite deposits with kaolinite, gypsum a.o. Milton et al. (1955) have confirmed the presence of illite and other clayey material in the residual clays underlying pyritic Chattanooga shale (Upper Devonian). Basaluminite occurs there in association with different Al, Fe and Ca hydrated sulphates.

GEOLOGIC ENVIRONMENTAL CONDITIONS

It may be inferred from the only occurrence of basaluminite in the Polish Flysch Carpathians (1 km to NE from village Sienna, on the shore of dam-lake Rożnów) that a number of special factors are needed for the formation of this mineral. One of the most important agents is the adequately high content of pyrite in rocks, as evidenced in some shales of the Hieroglyphic beds (Upper Eocene). The decomposition of pyrite is the only possible source of strong acid — sulphuric acid. Equally important seems to be the kind of clay mineral assemblage which besides illite should comprise the most solvable and richest in alumina mineral — kaolinite. It must be emphasized too, that the surplus content of carbonates in shales (calcite and magnesian calcite in examined rocks) will minimize in high degree the action of sulphuric acid used for the neutralization of alkali-earth carbonates favouring the basic Al-sulphate formation. Simultaneously, the decreasing acidity of solution favours the coagulation of silica-alumina gel (at pH = 4 for allophane).

Not without significance are the hydrodynamic conditions of ground-waters occurring, e.g., in mildly wet climate. There are many signs of drainage by valley- or strata-sources within slopes descending immediately to the dam-lake. Excessively vivid circulation of waters, as well as, much restricted one are equally unfavourable. In the first instance relatively easily soluble Al-sulphates could not be precipitated, and in the second the division of silica gel and alumina salts will not take place. Some influence on the diffusion and filtration gradients must be attributed to the seasonal oscillations of water-level in the dam-lake. Not without importance is the local continually changing humidity of air; the temperature conditions are probably insignificant.

With the varying degree of dilution of ground-waters and their contamination alter the pH and E_h parameters. The fissures in coarser grained sediments, only some centimetres distant, belong to three mutually perpendicular systems and facilitate the permeation and deposition phenomena, which are still active.

PHYSICAL AND CHEMICAL PROPERTIES

Microscopic examination. Powdery and compact or dense varieties of white to faintly yellowish brown sulphate mineral with dull, chalky luster appear both as coatings on walls of outcropping sandstone and mudstone intercalations or as crack and joint infillings penetrating

these rocks. Examined under microscope the air-dried material exhibits always a microcrystalline structure of nodular or globular aggregates composed of radially, feathery or sheaf-like ordered or disordered laths and fibres. The sub- or euhedral, cleavable crystallites may reach up to 90, normally 20 μm in length and 1—2 μm in breadth, against usually noted length up to 5 μm . The globules with mosaic, disordered structure, up to 80—90 μm in diameter originated from dehydration of hydrobasaluminite preserved elsewhere in radially ordered, fibrous aggregates. Hydrobasaluminite was also observed as felt-like clusters of fibres penetrating allophane accumulations (nests and veinlets). In the same form appear gypsum crystals in rare examples.

The optic properties of basaluminite are uniform, characterized in bulk by light grey interference colours, straight extinction, and negative sign of elongation ($n_a \parallel$ to elongation) of fibers and laths. The refractive indices measured in Na-light amounted:

$$n_a = 1,513 - 1,514 \pm 0,001 \text{ and } n_\gamma = 1,523 \pm 0,001$$

These values are well comparable with those obtained by Hollingworth and Bannister ($n = 1,519$), Tien ($n = 1,520$), Frondel ($n = 1,525$), Fominyh ($n = 1,520$) and Sunderman and Beck ($n = 1,512$ to 1,517). Mean index of refraction calculated by the Gladstone-Dale law (Tien, 1968) equals 1,539. The index of refraction of hydrobasaluminite from Sienna is much lower, reaching only 1,482.

X-ray examination. Powdered, air-dried samples of basaluminite, gibbsite and allophane were separated and X-rayed in a Debye-Scherrer camera using Ni-filtered copper radiation or by the diffractometer technique (Rigaku-Denki apparatus) with the same filter and radiation. The X-ray patterns of examined basaluminite from Sienna were tabulated (Tab 1) together with those displayed by Hollingworth and Bannister (1950), Tien (1968), and Fominyh (1965). The coincidence of d-spacings and intensities is quite remarkable. The reflections derived from detrital quartz admixture, utilizable for verification of diffractogram, were omitted. No other X-ray lines, bands or haloes of different minerals were detected, proving high purity of studied specimen. In the associated allophane the X-ray patterns of rare hydrobasaluminite, basaluminite and common gibbsite are well discernable.

Thermographic and infrared adsorption data. The presence of adsorbed water, constitutional molecular water or hydroxyl groups affects the physico-chemical properties of minerals. These influences emerge from differential thermal curves and infrared absorption spectra in much suggestive manner. As might be expected the basaluminite possesses all the mentioned kinds of water.

In the differential thermal analysis of basaluminite from Sienna (Fig. 1, curve C) the endothermic peaks at 135°, 180°, 220°, 320°—355°, and 960°C could be distinguished. They correspond well to the extrema at 125°, 170°, 220°, 355°, and 940°C recorded by Tien (Fig. 1, B) or at 150°, 220°, 340°, and 880°C given by Fominyh. They may be interpreted as follows: dehydration affecting adsorbed and partly constitutional molecular water has its maximum at 125—135°C, whereas the remaining part of molecular water disappears at 150—180°C, simultaneously with the con-

Table 1

X-ray powder data for basaluminites

| Sienna | | Irchester* | | Crawford Co** | | Ural Mts.*** | |
|--------|------------------|------------|------------------|---------------|------------------|--------------|------------------|
| d(A) | I/I ₀ | d(A) | I/I ₀ | d(A) | I/I ₀ | d(A) | I/I ₀ |
| 9,38 | 100 | 9,4 | 8 | 9,30 | 8 | 9,12 | 2 |
| 7,88 | 2 | — | — | 7,81 | 2 | — | — |
| 7,32 | 10 | 7,18 | 1 | 7,30 | 5 | — | — |
| 6,81 | 12 | 6,73 | 3 | 6,80 | 5 | 6,90 | 1 |
| 5,90 | 20 | 5,92 | 5 | 5,90 | 6 | 5,92 | 1 |
| 5,31 | 17 | 5,27 | 5 | 5,30 | 5 | 5,33 | 1 |
| 5,00 | 5 | — | — | 4,99 | 3 | — | — |
| 4,687 | 55 | 4,68 | 7 | 4,67 | 7 | 4,70 | 6 |
| 4,133 | 3 | — | — | 4,13 | 1 | — | — |
| 3,862 | 6 | 3,87 | 5 | 3,88 | 5 | — | — |
| 3,685 | 25 | 3,68 | 6 | 3,65 | 6 | 3,66 | 3 |
| 3,618 | 3 | — | — | — | — | — | — |
| 3,436 | 8 | 3,44 | 5 | 3,43 | 6 | 3,44 | 3 |
| 3,228 | 6 | 3,20 | 2 | 3,22 | 3 | — | — |
| 3,137 | 3 | — | — | 3,14 | 1 | — | — |
| 2,945 | 4 | 2,90 | 3 | 2,94 | 4 | 2,93 | 1 |
| 2,830 | 7 | 2,82 | 3 | 2,83 | 4 | 2,82 | 1 |
| 2,714 | 9 | 2,71 | 4 | 2,72 | 5 | 2,71 | 3 |
| 2,549 | 3 | — | — | 2,55 | 1 | — | — |
| 2,465 | 10 | 2,45 | 4 | 2,46 | 4 | 2,43 | 1 |
| 2,387 | 3 | 2,38 | 2 | 2,39 | 1 | — | — |
| 2,265 | 12 | 2,26 | 5 | 2,28 | 5 | 2,27 | 4 |
| 2,191 | 8 | 2,18 | 4 | 2,177 | 6 | 2,185 | 4 |
| 2,069 | 3 | 2,06 | 3 | 2,072 | 2 | 2,06 | 2 |
| 2,034 | 5 | 2,02 | 3 | 2,036 | 3 | 2,02 | 2 |
| 1,965 | 2 | 1,953 | 2 | 1,963 | 3 | 1,957 | 1 |
| 1,887 | 20 | 1,880 | 6 | 1,886 | 6 | 1,876 | 5 |
| 1,842 | 3 | 1,835 | 4 | 1,841 | 3 | 1,839 | 2 |
| 1,770 | 8 | 1,762 | 4 | 1,770 | 4 | 1,767 | 2 |
| 1,684 | 1 | 1,673 | 2 | 1,682 | 1 | — | — |
| 1,617 | 4 | 1,616 | 4 | 1,623 | 4 | 1,620 | 3 |
| 1,573 | 1 | — | — | 1,571 | 1 | — | — |
| 1,468 | 2 | 1,462 | 2 | 1,4685 | 2 | 1,461 | 1 |

* Lodge pits, Irchester, Northamptonshire, England (Hollingworth & Bannister, 1950).

** Crawford County, Kansas, USA (Pei-Lin Tien, 1968).

*** Kaluginskoye ore district, Ural Mts. USSR (Fominyh, 1965).

version of basaluminite to meta-basaluminite with chemical formula $Al_4SO_4(OH)_{10}$. It was primarily postulated by Hollingworth and Bannister as being accomplished at 150°C (after X-ray data) or at 75° to 185°C according to Tien's opinion. Sunderman and Beck pointed out the stability of meta-basaluminite until 200°C at which temperature it started to decompose in amorphous material, losing contemporaneously the ability to rehydroxylation. The peaks at 220° and 340—355°C correspond to the dehydroxy-

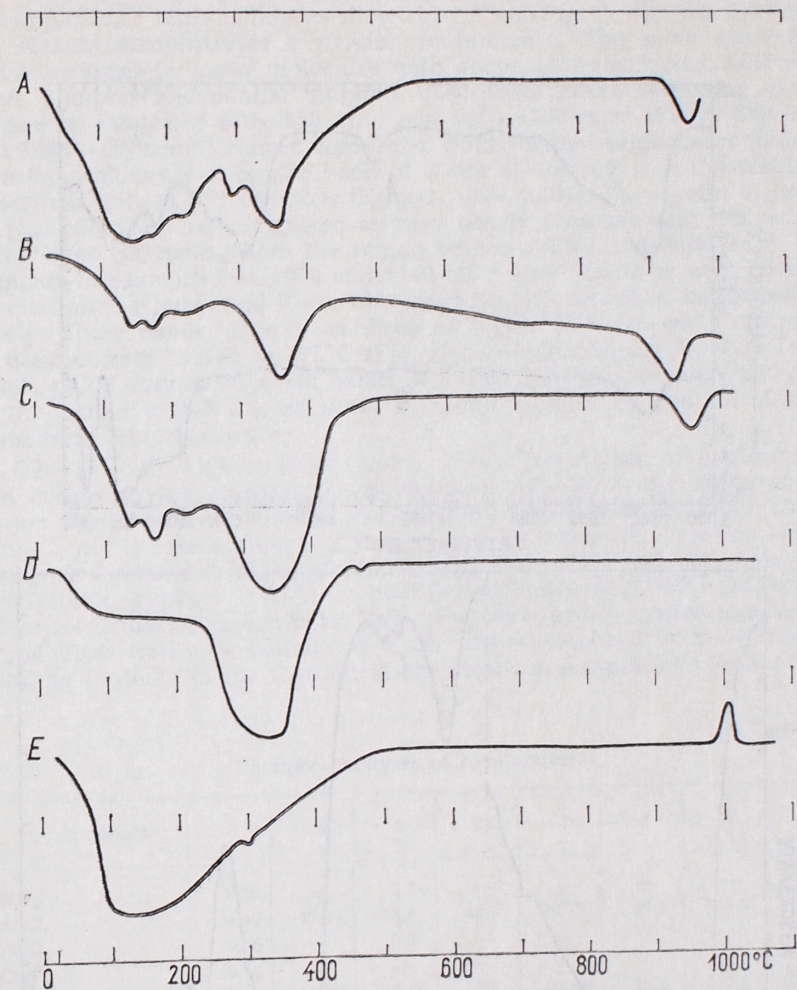


Fig. 1. Differential thermal curves of: basaluminite intergrown with gibbsite and allophane from Hieroglyphic beds, Sienna, Carpathians (A); basaluminite from Cabaniss formation, Kansas (Tien, 1968) (B); basaluminite, Sienna (C); gibbsite, Sienna (D); allophane with a small amount of gibbsite, Sienna (E)

lation, advancing in two stages. The last stage must be attributed to the collapse of the octahedral, gibbsite-like(?) sheets. This view can be supported by the similar dehydroxylation temperature of gibbsite (Fig. 1, D). Samples heated by Tien to the temperatures between 200° and 1050°C did not rehydrate to basaluminite within two months time. After Sunderman and Beck the poorly crystalline Al_2O_3 forms in the range 940—1000°C, preceded by endothermic sulphate dissociation.

Infrared absorption spectrum of basaluminite from Sienna (Fig. 2, C)

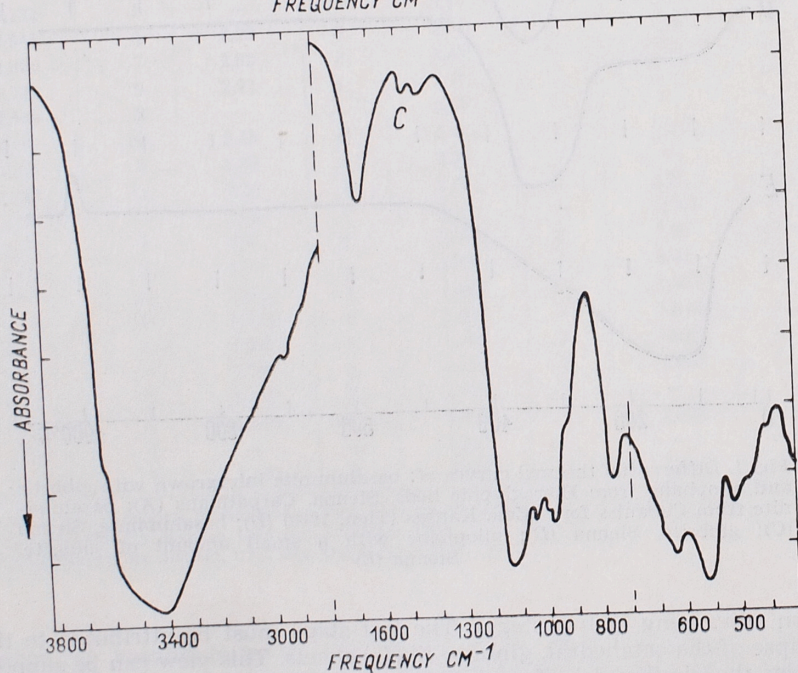
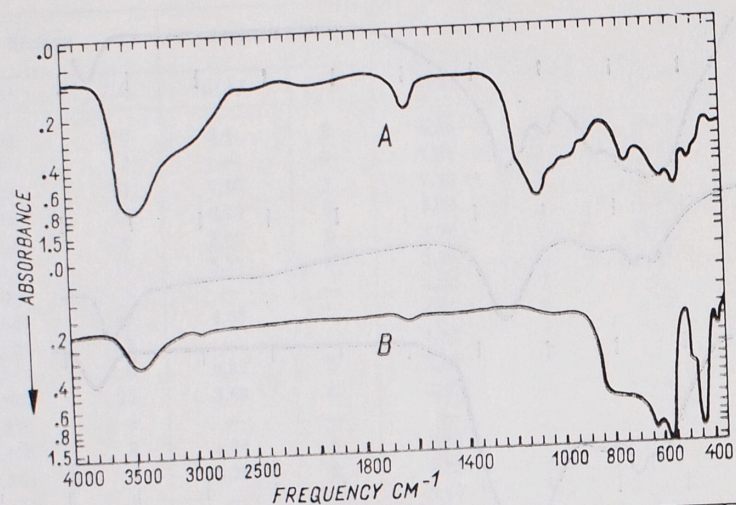


Fig. 2. Infrared absorption spectra of basaluminite (A) and heated (to 975°C) basaluminite (B) from Cabaniss formation, Kansas (Tien, 1968) in comparison with spectrum of basaluminite from Hieroglyphic beds at Sienna (C)

in comparison * with analogous showed by Tien (Fig. 2, A) from Crawford Co, Kansas demonstrates a striking resemblance. The same absorption bands assigned to water molecules with about 1630 cm^{-1} , and 2930 cm^{-1} wave numbers and similar sulphate absorption bands extending in the frequency ranges of 570—650 cm^{-1} and 990—1180 cm^{-1} (Tien's 580—670 and 1050—1200 cm^{-1} ranges resp.) can yield further evidence of mineral identity. Relatively strong ν_2 band of water at 1630 cm^{-1} is the result of greater deficit of R^{3+} (Al) ions (Kubisz, 1972, p. 31). The ν_1 and ν_3 bands of H_2O could not be recognized as they nearly coincide with OH-stretching band occupying here the region between 3200 and 3600 cm^{-1} . The sulphate bands with 990, 1050 and 1140 cm^{-1} wave numbers may possibly be attributed (Omori and Kerr, 1963) to S_2O_5 , SO_4 and S_2O_3 bands respectively. These bands, as well as those in region 570—650 cm^{-1} disappear in basaluminite heated to 975°C (Fig. 2, B). Remembering Pei-Lin Tien's (1968, p. 73) statement, weak bands of water, e.g., in 1630 and 2930 cm^{-1} in the heated to 975°C basaluminite, should indicate the content of some secondarily absorbed water.

Chemical investigations. Three specimens of basaluminite and accompanying minerals from Sienna were chemically analyzed for major elements. The chemical composition of basaluminite from Sienna (Tab. 2, no. 1) corresponds to a rather pure representative, except for the mechanical admixture of quartz (6.20 weight per cent) and simultaneously precipitated gypsum (1.34%) or goethite hydrolysate (0.60%) impurities. After recalculation (column 1a, Tab. 2) appears some surplus quantity of alumina, as well as a deficit in water when compared with the corresponding contents in the theoretical chemical composition of basaluminite:

Table 2

Chemical analyses of basaluminites

| Components | 1 | 1a | 2 | 2a | 3 | 4 | 5 | 6 |
|-------------------------|--------|--------|-------|-------|-------|-------|-------|-------|
| SiO_2 | 6.20 | — | 2.4 | — | — | — | — | 0.37 |
| Al_2O_3 | 44.49 | 48.43 | 43.0 | 43.5 | 39.70 | 47.1 | 45.8 | 44.08 |
| Fe_2O_3 | 0.45 | — | 0.3 | — | — | — | — | 0.07 |
| CaO | 0.44 | — | — | — | — | — | — | — |
| SO_3 | 16.86 | 17.68 | 15.6 | 17.4 | 20.06 | 15.5 | 17.3 | 16.72 |
| H_2O | 31.56 | 33.89 | 38.7 | 39.1 | 39.94 | 37.4 | 36.9 | 38.53 |
| Total | 100.00 | 100.00 | 100.0 | 100.0 | 99.70 | 100.0 | 100.0 | 99.82 |

1. and 1a. Specimen from Sienna, Carpathians, Poland; weight percentages before (1) and after (1a) recalculation; H_2O content by difference.
2. and 2a. Lodge pits, Irchester, Northamptonshire, England (Hollingworth & Bannister, 1950); before (2) and after (2a) recalculation.
3. Mount Bernon, Epernay, France (fide Hollingworth & Bannister, 1950); recalculated excluding 0.3% of CaSO_4 .
4. and 5. Crawford County, Kansas, USA (Pei-Lin Tien, 1968); recalculated excluding 1.4% SiO_2 , 1.0 Fe_2O_3 , 2.4—1.0% CaO , 0.1% MgO and 0.1% K_2O .
6. Shoals, Indiana, USA (Sunderman & Beck, 1969); with 0.021% of P_2O_5 .

* The absorption spectra were obtained with Zeiss UR-10 spectrophotometer, using KBr prism, KBr pellet and 0.25—0.31% sample content. Tien applied Perkin-Elmer (Model 521) spectrophotometer and KBr disks, containing about 0.3% sample.

Table 3

Chemical analyses of gibbsite and allophane

| Components | Gibbsite | | | Allophane | | |
|--|--------------------|-----------------------|------------|--------------------|-----------------------|------------|
| | Weight % | Weight % ¹ | Mol. ratio | Weight % | Weight % ² | Mol. ratio |
| SiO ₂ | 3.34 | — | — | 22.58 | 25.22 | 1.259 |
| Al ₂ O ₃ | 57.94 | 63.57 | 1 | 30.43 | 33.99 | 1 |
| Fe ₂ O ₃ | 1.37 | — | — | 2.51 | — | — |
| CaO | 0.67 | — | — | 2.38 | — | — |
| SO ₃ | 0.43 | — | — | 3.26 | — | — |
| H ₂ O ⁻ | 2.39 | — | — | 22.13 | — | — |
| H ₂ O ⁺ | 33.86 ³ | 36.43 ³ | 3.243 | 16.71 ³ | 16.07 ³ | 6.791 |
| Total | 100.00 | 100.00 | | 100.00 | 100.00 | |

¹ Recalculated excluding detrital quartz (3.34 weight %), goethite (1.83%), gypsum (0.92%), H₂O⁻ 105°C (2.39%) and surplus CaO (0.37%).

² Recalculated excluding goethite (3.36%), gypsum (7.01%) and surplus CaO (0.10%).

³ H₂O⁺ content by difference.

Al₂O₃ = 44.0%; SO₃ = 17.2% and H₂O = 33.8 weight per cent. The differences may better be accentuated in form of molecular ratios Al₂O₃ : SO₃ : H₂O, amounting here: 2,152 : 1 : 8,519, in place of theoretical 2 : 1 : 10 proportion. Similar anomalies may be found in other specimens as in collected from Crawford Co (Tien, 1968). This is probably due to further continuing dehydration of basaluminite — Al₄SO₄(OH)₁₀ · 5H₂O. It must be emphasized that the admixture of gibbsite in basaluminite was not, as yet, detected by X-ray and other methods. Though the basaluminite is much more stable than the more hydrated equivalent — hydrobasaluminite (Al₄SO₄(OH)₁₀ · 31H₂O?), there are some indications suggesting the existence of less hydrated links in the dehydration process. This is especially possible in lowest humidity conditions, where meta-basaluminite (Al₄SO₄(OH)₁₀), obtained easily at 150°C, seems to be final stable variety.

The supplementary minerals in the paragenetic assemblage — gibbsite and allophane, judging from the demonstrated (Tab. 3) chemical analyses possess the identical mineral impurities of detrital quartz, goethite, and gypsum. In allophane some iron and calcium may occur in ionic, absorbed form. The same mode of occurrence can be implied in the case of SO₃ or correctly SO₄²⁻ anion, though in some cases basaluminite or hydrobasaluminite admixture was detected by X-ray method. The molecular ratio SiO₂ : Al₂O₃ : H₂O in allophane do not deviate much from normally noted, taking into account surplus of silica connected with detrital quartz in undeterminable amounts. The content of gypsum and goethite is considered rather as hypothetical, hence the selection and quantitative determination of separated minerals and their components was beyond the analytical possibilities.

GENETIC REMARKS

It has long been recognized by Bassett and Goodwin (1949) that the endeavour of basaluminite and hydrobasaluminite synthesis must fail. The

supposed relative positions of the solubility curves of basaluminite and gibbsite (Fig. 3) in the immediate neighbourhood of the water pole (at 25°C) prove their stable state in contact with extremely dilute solutions, more or less (resp.) acid. According to Bassett and Goodwin the formation of gibbsite is accelerated by the presence of sodium, while the crystallization of another polymorph — bayerite, favours the addition of ammonia.

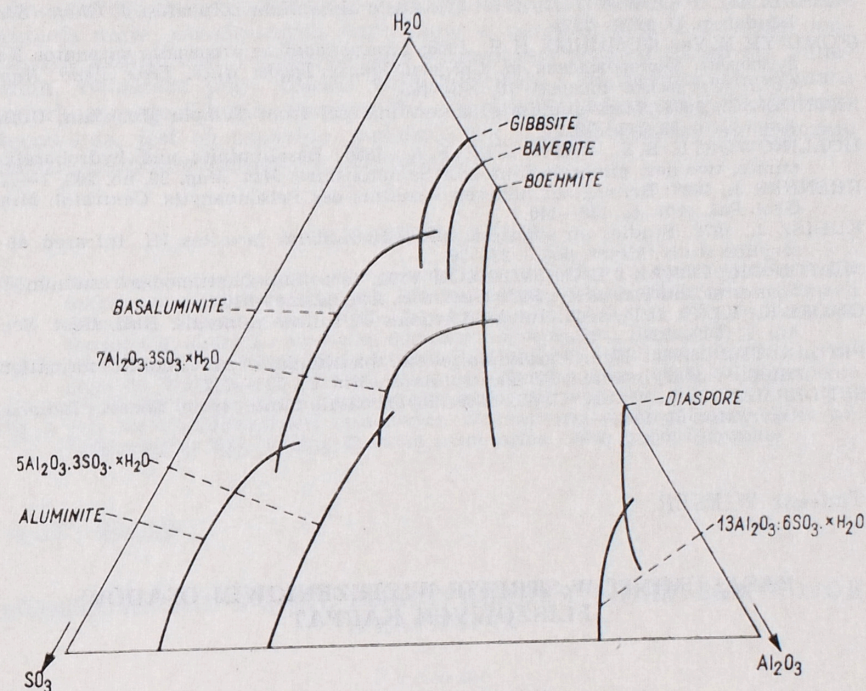


Fig. 3. The solubility curves of basic Al-sulphates and Al-hydroxides in the part nearest to the water pole. Modified after Bassett and Goodwin (1949)

The mentioned writers refer the coexistence of basic Al-sulphates and Al-hydroxide to the similarity of layer-lattice structures. The basaluminite structure should be considered as derivative from gibbsite structure in the same way the latter structure was derived from kaolinite structure.

Envisaging these circumstances, as well as the actually observed alternation of allophane, gibbsite and basic Al-sulphate intercalations and nests the replacement hypothesis becomes much suggestive. When the (hydro-) basaluminite — gibbsite reaction might be considered as reciprocal, allophane could not replace the basic Al-sulphate.

The relationship of the studied sulphates with the minerals felsönbanyite and paraluminite is doubtful and should be revised. The former mineral, described by Haidinger and Krenner (1928), is optically and chemically almost identical with the basaluminite. The well developed crystals and the paragenetic relations with stibnite and barite imply the elevated temperature of water solutions.

Acknowledgements. The author is much indebted to leaders of Institute of Mineralogy and Mineral Deposits of the Academy of Mining and Metallurgy in Cracow and X-ray Laboratory of Geological Institute in Warsaw for furnishing infrared absorption spectra and X-ray diffractograms, resp.

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BASALUMINIT W STREFIE WIETRZENIOWEJ OSADÓW FLISZOWYCH KARPAT

Streszczenie

W brzegu sztucznego Jeziora Rożnowskiego, koło wsi Sienna, został znaleziony basaluminit w towarzystwie hydrobasaluminitu, gibbsytu (hydrargilitu), alofanu, gipsu, uwodnionych tlenków Fe i Mn oraz, w dalszym sąsiedztwie — jarosytu. Basaluminit jest tam minerałem proskwowym lub zbitym, białym do jasno żółtawobrunatnawego, przy matowym, kredowatym połysku. Tworzy on powłoki lub wypełnienia szczelin we wkładkach piaskowcowych i mułowcowych tworzących wespół z łupkami kompleks warstw hieroglifowych (górną eocen).

Powstanie basaluminitu wiąże się ze źródłami warstwowymi, lub dolinnymi, usytuowanymi tuż nad zmiennym zwierciadłem jeziora. Kwas siarkowy z wietrzejącego pirytu i znaczny udział kaolinitu w zespole minerałów ilastych warstw hieroglifowych oto najważniejsze czynniki sprzyjające powstaniu basaluminitu i hydrobasaluminitu. Ten ostatni jest zapewne niezbędnym ogniwem w procesie tworzenia się basaluminitu na drodze dehydratacji. Oba zasadowych siarczanów glinu nie udało się zsyntetyzować przez wytrącenie z roztworu. Należy przypuszczać, że są to produkty zastąpienia gibbsytu i alofanu (zawierającego zawsze domieszkę

gibbsytu) za sprawą bogatych w kwas siarkowy wód gruntowych. Zasadowe siarczanu glinu mogą hydrolizować przechodząc w gibbsyt (reakcja odwracalna).

Rozbiory chemiczne basaluminitów dowodzą, że minerały te mogą zawierać nadmiar glinki i wykazywać równocześnie niedobór wody, wskutek hydrolizy i dehydratacji w mniej uwodnione odmiany. Cechy fizyczne nie ulegają przy tym zmianom wykrywalnym metodami rentgenograficznymi, termograficznymi czy absorpcji w podczerwieni. Możliwa jest także rehydratacja mniej uwodnionych siarczanów w bardziej bogate w wodę, jakkolwiek basaluminity wydaje się być stosunkowo wysoko stabilnym minerałem, zwłaszcza przy niskich wilgotnościach i temperaturach klimatu umiarkowanego. Chociaż znany tylko z mniej niż dziesięciu punktów występowania, jest on zapewne, podobnie jak i hydrobasaluminity, znacznie bardziej rozpowszechniony w przyrodzie.

OBJAŚNIENIA FIGUR

- Fig. 1. Krzywe termiczne różnicowe: przerostów basaluminitu z hydrargilitem i alofanem z warstw hieroglifowych, Sienna, Karpaty (A); basaluminitu z formacji Cabaniss, Kansas (Tien, 1968) (B); basaluminitu, Sienna (C); hydrargilitu, Sienna (D); alofanu z niewielką domieszką hydrargilitu, Sienna (E)
- Fig. 2. Widma absorpcyjne w podczerwieni basaluminitu (A) i basaluminitu ogrzanego do 975°C (B) z formacji Cabaniss, Kansas (Tien, 1968) w zestawieniu z widmem basaluminitu z warstw hieroglifowych w Siennej (C)
- Fig. 3. Krzywe rozpuszczalności zasadowych siarczanów i wodorotlenków Al w pobliżu punktu H₂O, według Bassetta i Goodwina (1949, zmodyfikowane)

Tadeуш WIESEP

БАЗАЛЮМИНИТ В ЗОНЕ ВЫВЕТРИВАНИЯ ФЛИШЕВЫХ ПОРОД В КАРПАТАХ

Резюме

На склоне Рожновского водохранилища в районе с. Сенна был найден базальюминит в сопровождении гидробазальюминита, гиббсита (гидраргиллита), аллофана, гипса, гидроокислов железа и марганца, а также на некотором расстоянии ярозита. Базальюминит представляет здесь порошкообразную или плотную массу белого до светложелто-буроватого цвета, с матовым, меловым блеском. Он образует каемки или выполняет трещины в прослоях песчаников и алевролитов, которые совместно со сланцами слагают комплекс иероглифовых слоев (верхний эоцен).

Базальюминит образовался под влиянием межпластовых или долинных источников, находящихся выше переменного зеркала воды в водохранилище. Основными факторами, которые благоприятствовали образованию базальюминита и гидробазальюминита, было присутствие серной кислоты, образующейся за счет выветривания пирита, и повышенное содержание каолинита в комплексе глинистых минералов иероглифовых слоев. Гидробазальюминит представляет, вероятно, обязательное промежуточное звено на пути образования базальюминита в процессе дегидратации. Не удалось получить этих двух основных сульфатов алюминия путем синтеза из раствора. Следует предполагать, что они представляют

продукт замещения гиббсита и аллофана (всегда содержащего примесь гиббсита) под влиянием грунтовых вод обогащенных серной кислотой. Основные сульфаты алюминия вследствие гидролиза могут переходить в гиббсит (обратимая реакция).

Химический анализ базальюминитов показывает, что эти минералы могут содержать некоторый избыток глинозёма при одновременном недостатке воды вследствие гидролиза и дегидратации. При этом физические свойства не изменяются в такой степени, которую можно обнаружить методами рентгенографическими, термографическими или ИК-спектрами поглощения. Возможна также регидратация менее гидратированных сульфатов с их переходом в разности более богатые водой, хотя базальюминит является сравнительно стабильным минералом, особенно в условиях небольшой влажности и небольших температур умеренного климата. Базальюминит, как и гидробазальюминит, известен по нескольким местонахождениям, однако, кажется, что он более широко распространен в природе.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Кривые дифференциального термического анализа: прорастаний базальюминита с гидраргиллитом и аллофаном, иероглифовые слои, Сенна, Карпаты (А); базальюминита формации Кабанисс, Канзас (Тьен, 1968) (В); базальюминита, Сенна (С); гидраргиллита, Сенна (D); аллофана с небольшой примесью гидраргиллита, Сенна (Е)
- Фиг. 2. ИК-спектры поглощения базальюминита (А) и базальюминита нагретого до 975° (В), формация Кабанисс, Канзас (Тьен, 1968), в сопоставлении со спектром базальюминита из иероглифовых слоев, Сенна (С)
- Фиг. 3. Графики растворимости основных сульфатов и гидроокислов алюминия вблизи точки H_2O , по Бассету и Гудвину (1949), модифицированные