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Foreword

The Faculty of Natural Sciences and Mathematics, in the framework of scientific and academic activities, has decided to launch the second volume and issues 3 and 4 of the *Journal of Natural Sciences and Mathematics* of UT.

The scientific contributions in issues 3 and 4 are papers selected from the first International Scientific Conference organized by the Faculty of Natural Sciences and Mathematics, which successfully carried out its activity on 16 June 2017, in the premises of the University of Tetova. This conference proved to be a gathering that brought together well-known experts to discuss the latest research achievements, perspectives of future developments and innovative applications in the field of computer science, maths, physics, chemistry, biology, geography and ecology.

We show special consideration to all those authors from the country and abroad who honored us with their scientific participation at our faculty's conference and publishing their contributions in the *Journal of Natural Sciences and Mathematics* of UT, which is firmly striding toward the heights of science and knowledge in the field of natural science.

Editor-in-chief

Prof. Dr. Vullnet Ameti

Content

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Original scientific paper

Phase relations between Baryte – $BaSO_4$, cymrite – $BaAl_2Si_2O_8 \cdot H_2O$ and Hyalophane – (K, Ba) Al Si_3 O_8 from the ore occurrence no. 2 at Kalugjeri micro-locality near Nezhilovo village, Macedonia

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Abstract

In the paper are shown results of the mutual phase relations between the Ba-minerals of hydrothermal origin, as follows: baryte, cymrite, and hyalophane from the aforementioned micro-locality, Macedonia. Baryte, cymrite, hyalophane were examined by the optical polarizing microscope, X-ray diffractometer and SEM-method. Cymryte is the oldest hydrothermal mineral between the mentioned groups of Ba-minerals and consequently it was metasomatic corroded, replaced by the younger baryte, hyalophane. Cymrite was discovered in the so-called quartz-cymrite and cymrite-quartz schists. The phase relations between baryte and cymrite were examined in the contact area between baryte and quartz-cymrite schists that's in the so called baryte-cymrite schists. The phase relations between cymrite-hyalophane were examined inside hyalophane-cymrite lense like body enclosed inside the quartz-cymrite schists.

Keywords: baryte; cymrite; hyalophane; phase relations.

Introduction

The hydrothermal mineral associations of Ba-minerals (baryte, cymrite, hyalophane) at Kalugjeri micro-locality are quite well known according to the earlier examinations (D. Nikolić, 1958; Lj. Barić, 1960; S. Jančev, 1975, 1982, 1994). The aforementioned minerals are originated during a wider temperature span inside the progress of the hydrothermal stage of crystallization. In spite of the highest temperature mineral paragenesis (gahnite, franklinite, zircon, zincochromite etc.) characterized with fine-grained forms and structures, the examined Ba-minerals of hydrothermal origin (baryte, cymrite, hyalophane) are found in coarse-grained forms in different generation.

Methods of investigation

- The geological prospection was actually the most important methodological approach in this work especially of mineral collecting point of view inside the so called baryte-cymrite and hyalophane-cymrite schists.

- Microscope polarizing methods (SM-POL, Leitz, Wetzlar, Germany) in transmitted and reflected light, X-ray diffractometer (Philips instrumentation) and micro-probe (Jeol, SEM) examinations were performed for baryte, cymrite, hyalophane examinations.

1. Geological setting

The ore occurrence N_0.2 at Kalugjeri micro-locality (S.Jančev, 1979) was described as a peculiar ore occurrence of baryte schists enclosed in the dolomite marbles with complex-pollymetallic mineral parageneses composed of gahnite, franklinite, Pb-bearing piemontite, nezhilovite, quartz, Zn-rich phlogopite, quartz, siderite, hematite etc. In the footwall of the baryte schists were discovered contact baryte-cymrite schists and underlying quartz-cymrite, cymrite-quartz schists (Fig.1).

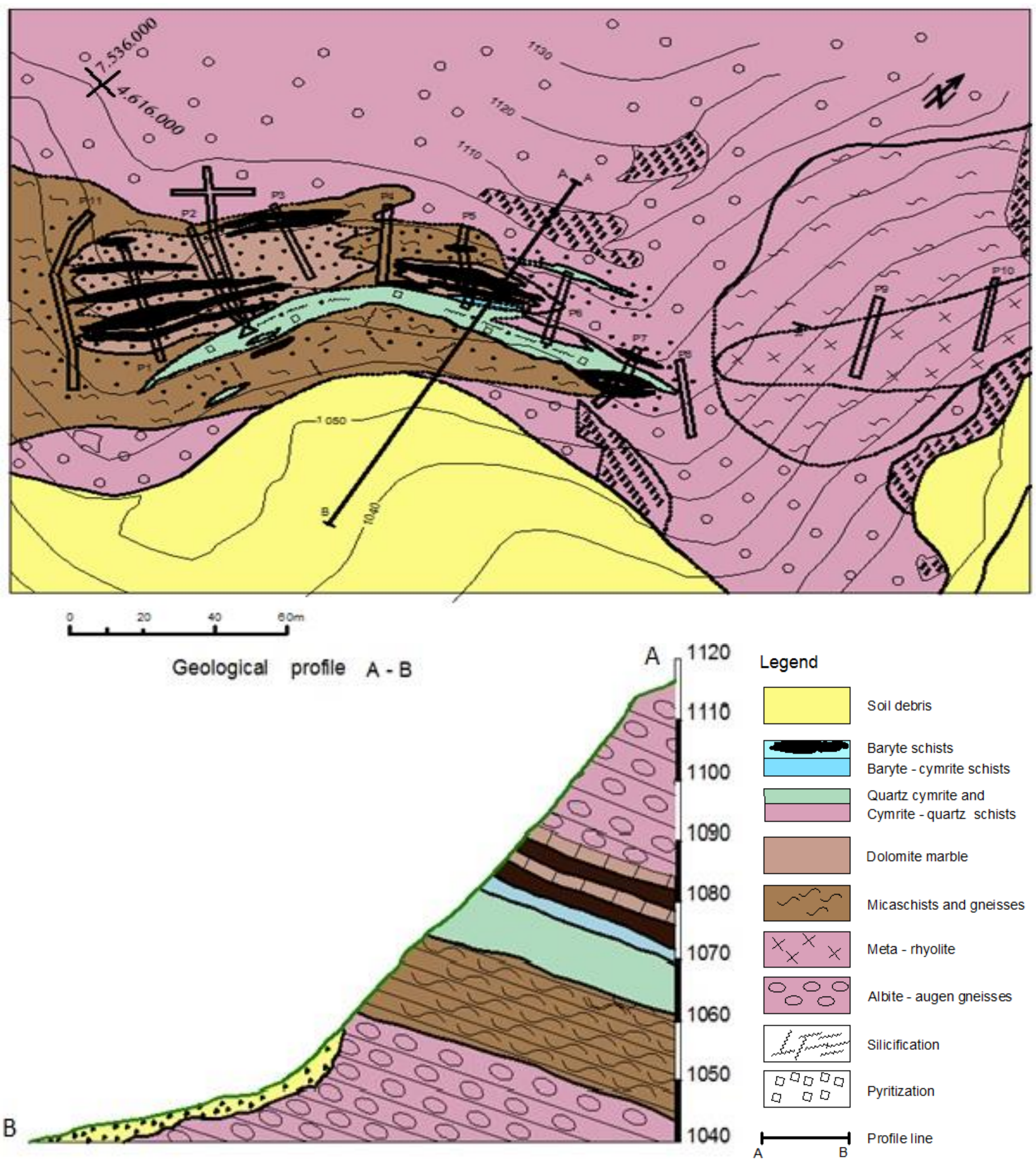

Fig.1 Geological map of the ore occurrence N_0.2 at Kalugjeri micro-locality

Later (S. Jančev, 1994) were discovered hyalophane-cymrite schists as lens like body of very limited dimensions (about 1m long with 0,3m thickness) enclosed in quartz-cymrite schists.

So, along the profile line A-B (and very close to the trench P-5) were collected samples of baryte-cymrite and hyalophane-cymrite schists in very important points where are reported the mutual phase relations between baryte, cymrite and hyalophane.

2. Mineralogical-petrographical description

A. Baryte and baryte-cymrite schists

Baryte schists are middle to fine-grained rocks with light bluish (nearly white color) composed mainly of baryte (in variable quantities of 40-50 % to 80-100 %) as predominant mineral and other subordinates or accessories as follows: muscovite - phengite, biotite, Zn - rich phlogovite, Mn - muscovite, quartz, hematite, spesartite, nežilovite, hematite, gahnite, franklinite, hedyphane etc. Baryte grains are irregular of 0,1–0,3 mm. to 1-2 mm.

Baryte was determined by chemical (D. Nikolić, 1959), optical (2V=39 - 46°), X-ray powder method (-d-A – 4,29; 3,893; 3,342; 3,091; 2,843; 2,733; 2,103).

Mass-spectrometric examinations show variable ^{34}S values of about +21 ‰ to +28 ‰ instructing to a S-source of marine origin.

In the lowest parts (that's contact parts of the baryte schists with quartz-cymrite schists) in the baryte schists was discovered cymrite (in variable amounts of cca 10-20%) and consequently they represent actually baryte-cymryte schists. This contact part of baryte-cymrite schists with thickness of cca 0,3 m.-0,5 m. is very important part because in these schists are visible the mutual phase relations between baryte and cymrite. **Namely, by means of the microscopic examinations were determined the mutual phase relations between the older cymrite and the younger baryte crystals. Cymrite grains are partially replaced with the younger baryte during the metasomatic processes inside the low-temperature hydrothermal stage (Fig.2; 3).**

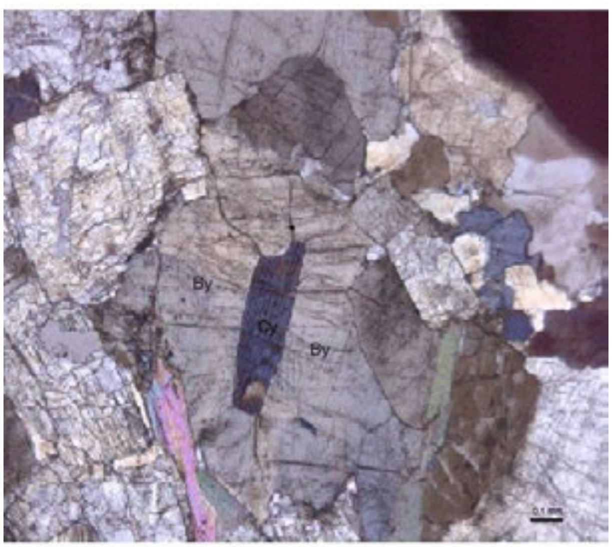

Fig.2 Metasomatic replacements of the older cymrite (cy) by the younger baryte (by); (N +)

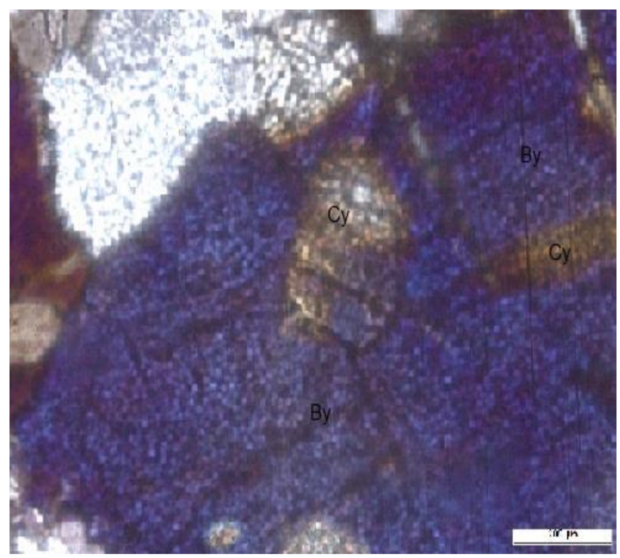

Fig.3 Corroded, rounded relic of cymrite (cy) by the younger baryte (by); (N +)

According to X-ray powder examinations, in the contact barite - cymrite schists were confirmed barite-cymrite mineral associations (Fig.4).

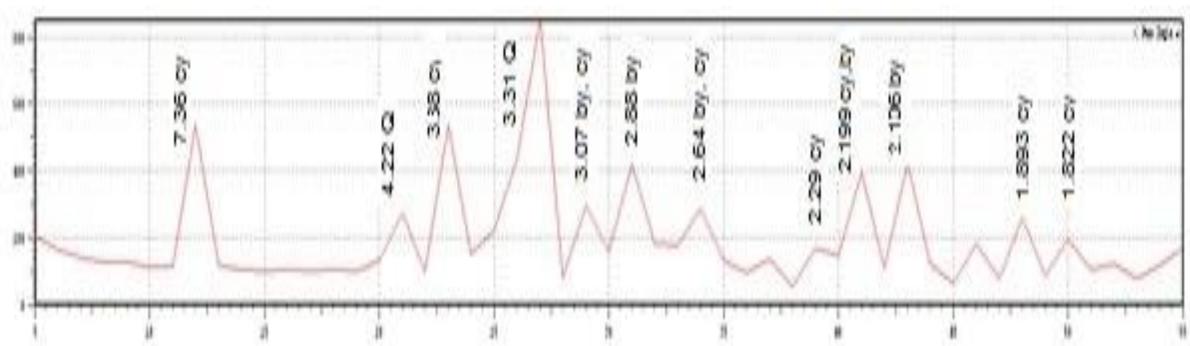

Fig.4 X-ray powder diffractogram of baryte (by) - cymrite(cy) schist and quartz (Q)

B. Quartz-cymrite and cymrite-quartz schists

In the footwall of the baryte and baryte-cymrite schists were discovered quartz-cymrite and cymrite-quartz schists (S. Jančev, 1975). Cymrite was determined by optical (2V = 8-10°; w= 1,6103; E=1,6011) and X-ray diffractometer method (-d- Å 7,66; 4,61; 3,94; 3,83; 2,952; 2,664; 2,557; 2,530; 2,307; 2,236; 2,211; 1,995; 1,921). Later cymrite was confirmed by chemical analysis - Table 1 (S. Jančev, 1989) and consequently was determined the empirical formula as follows:

$$(Ba_{0,86},K_{0,01})_{0,87}\ (Al_{1,83},Si_{0,17})_{2,0}\ Si_{2,05}O_8 \cdot H_2O$$

Common quartz-cymrite schist is composed (S. Jančev, 1989) of quartz, cymrite; muscovite but here and there in these schists can be found different minerals of minor importance or accessories as follows: titanite, galena, pyrite, rutile cleiophane, zircon, baryte, unusual tourmaline (with very strange pleohroitic colors).

C. Hyalophane-cymrite schists

According to earlier examinations (S. Jančev, 1994) in the mixed series at the ore occurrence N_0.2 at Kalugjeri micro-locality, were discovered hyalophane-cymrite schists as one local phenomenon (lense like body with very limited dimensions of cca 1 m. long and 0,3m.-0,5 m. thickness) enclosed in the quartz-cymrite schists. The microscopic examinations show that aforementioned schists are composed of hyalophane, muscovite, quartz, cymrite, biotite, titanite, baryte, pyrite and galena.

Hyalophane is quantitatively predominant mineral in the hyalophane-cymrite schists in comparison with subordinate cymrite, muscovite, and quartz. Hyalophane content in the treated schists vary of cca 50-60% to cca 80-90%. All hyalophane grains are always irregular (with size between 0,1-0,3 mm. to cca 1-1,5 mm.), muddy due to the weathering processes on potassium base and very intimately connected with subordinate minerals-quartz, cymrite, muscovite, baryte. In the coarse-grained hyalophane grains very often can be encountered very intensively metasomatic replacements of older cymrite grains by the younger hyalophane (Fig.5; 6).

The very markedly metasomatic corrosions and replacements between hyalophane over the older cymrite are so very intensively present in the treated rock because the very rare cymrite relics are barely visible by the polarizing microscop.

The other minerals-titanite, muscovite is also metasomatic replaced by the younger hyalophane. Hyalophane was determined for first time (S. Jančev, 1994) on a base of preliminary performed micro-probe analysis (by Sergei Korikowsky, IGEM, AN, Moscow) and consequently was determined the empirical formula as follows:

$$(K_{0,72},Ba_{0,16},Na_{0,08})_{0,96}\ (Al_{1,2},Si_{0,8})_{2,0}\ Si_2O_8$$

Fig.5 Cymrite (cy) relic very intensively metasomatic replaced by the younger hyalophane (hy); (N+)

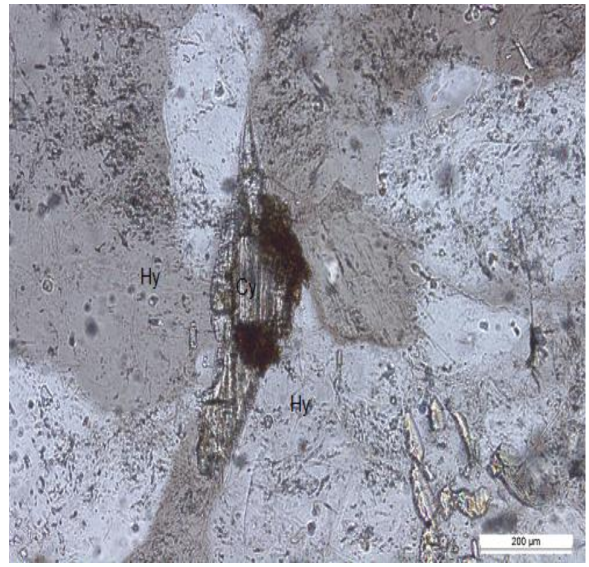

Fig.6 Very intensively metasomatic replaced and barely recognized cymrite (cy) relics by the younger hyalophane (hy);(N+)

According to the later micro-probe examinations (Table 1) hyalophane was determined at different points inside different crystals, as follows:

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO_2	55,22	52,08	50,24	52,79	53,17	52,28	49,51	35,46	30,54
Al_2O_3	20,99	21.41	21,35	20,47	20,71	21,23	25,48	24,77	25,91
BaO	13,99	14,93	15,08	12,47	11,96	13,36	11,47	35,32	38,97
ZnO	/	/	/	/	/	/	/	0,13	/
Na_2O	0,70	0,86	1,23	0,98	0,43	1,29	3,56	/	/
K_2O	12,47	11,35	11,32	12,39	13,29	11,68	9,98	0,15	/
Loss of ign.	/	/	/	/	/	/	/	4,2	4,58
Total	100,37	100,63	99,22	99,10	99,56	99,84	100,00	100,3	100,00

Table 1. Results of the micro-probe examinations for cymrite, hyalophane (%)

(1); (2); (3); (4); (5); (6) - Analyses at randomly selected points at different hyalophane crystals,

(7) - Hyalophane - literature data (Palache Ch., 1935),

(8) - Cymrite classical analisiss of Macedonian sample,

(9) - Cymrite - literature data (Benallt mine 1949 Walls, England).

On a basis of 8 -oxygen ions were calculated empirical formulas for hyalophane as follows:

(1) - $(K_{0,73}, Ba_{0,23}, Na_{0,042})_{1,00}\ Al_{1,0}\ (Si_{2,755}, Al_{0,24})_{2,995}O_8$

(2) - $(K_{0,67}, Ba_{0,29}, Na_{0,08})_{1,04}\ Al_{1,0}\ (Si_{2,72}, Al_{0,26})_{2,98}\ O_8$

(5) - $(K_{0,63}, Ba_{0,26}, Na_{0,125})_{1,015}\ (Si_{2,73}, Al_{0,26})_{2,99}\ O_8$

Hyalophane was confirmed also by means of X-ray powder analysis (d - A - 6,45; 4,60; 4,25; 3,80; 3,62; 3,48; 3,34; 3,01; 2,91; 2,58; 2,33; 2,22; 2,13). In Fig. 7 is presented X-Ray powder diffractogram of hyalophane-cymrite schist.

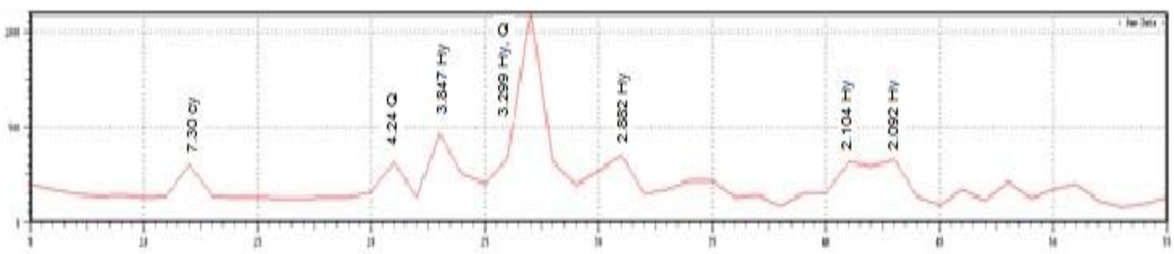

Fig.7 X-ray powder diffractogram of hyalophane (Hy) – cymrite (cy) schist and quartz (Q)

Hyalophane analyses of determined mineral from treated area show quite good and comparable results with literature data. Certain chemical deviations in the hyalophane results from Macedonia and results of literature data due to the different rates of isomorphic substitutions between K and Ba.

Cymrite analysis from Macedonian sample show quite good results which are comparable with literature data. In Macedonian cymrite sample there is certain increased SiO_2 - contents of 5 % consequently to the presented quartz inclusions in the treated cymrite crystals from Macedonia.

3. Discussion and conclusions

Cymrite as a new mineral species was discovered in the Benallt manganese mine, Wales (Campbell Smith et. all., - 1949). Cymrite from Macedonia was discovered in Nezhilovo village area (Jančev S., 1975). Starting from 1949 to this day, cymrite was discovered in more than 30 different localities in the world. Cymrite - hyalophane - baryte mineral associations are discovered only in several micro-localities in the world (Wales - Campbell S., et. all - 1949; Switzerland- Stalder, H.A., et. all., 1998; Spain - Maria C. Moro et. all, 2001) in quite different geological, geochemical, mineralogical - petrological, geochronological ets. circumstances. Starting from the aforementioned cymrite – hyalophane - barite - mineral associations and their phase relations from the treated area could not be compared with the same mineral associations from Wales, Spain and Switzerland.

Nevertheless, we could accept one literature data (Maria C. Moro et. all, 2001) that cymrite forming from Macedonia is probably favorized at low T (350-370°C) and low P (1,5 kb) in metasedimentary environments at increased H_2O partial pressures. Cymrite from Macedonia is also originated in conditions of high barium activities according to the paper by Sorokhtina, N.V. et. all, 2008.

A very important and common characteristic for the very rare and very complex mineral parageneses (zircon, zincochromite, franklinite, gahnite, hetaerolite, nežilovite, rinmanite, epidote-(Pb), Pb-bearing piemontite, piemontite - (Pb), ferricoronadite, zincohoegbomite, Fe-analogue of zincohoegbomite, Mn-analogue of plumboferrite, Zn-rich egirine-augite, Zn-rich phlogopite, Zn-rich magnesioriebeckite, amazonite, tilasite, cymrite, baryte, hyalophane, hedyphane, calcite, dolomite, quartz etc.) determined in the ore occurrences of the mixed series near Nezhilovo village is presented by the very complex mutual phase relations between different minerals of the aforementioned list of minerals due to the metasomatic processes.

So for example, inside the highest temperature mineral paragenesis (characterized with very fine-grained mineral associations and very fine-grained structures) were reported very intensively metasomatic replacements between the minerals of the rare spinel group (for example franklinite and hetaerolite are replaced by younger gahnite).

The mutual phase relations between baryte-cymrite hyalophane are given as follows:

During the low temperature hydrothermal stage, the older cymrite was metasomatic replaced by baryte in the mentioned baryte–cymrite schists. Cymrite was also corroded and metasomatic replaced by the younger hyalophane in the so called hyalophane-cymrite schists according to the metasomatic processes during the hydrothermal stage.

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