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**HARMOTOME IN MELABASALT FROM BIAŁA WODA
GORGE, PIENINY MOUNTAINS (POLAND)**

Abstract. Calcite amygdales dispersed in a melabasalt forming olistolithic block in the Jar-muta Conglomerate (Senonian) of Pieniny Klippen mantle are sometimes lined by small crystals of harmotome and occasional pyrite. Intensively salmon-red to flesh-red coloured zeolite appears as simple twins of morvenite type, as well as fourlings of the Marburg type. On account of restricted quantity of material only X-ray diffractometric, infrared spectroscopic and optical examinations were executed. Together with specific gravity determinations they indicate the appurtenance to Ba-rich member of the phillipsite-harmotome isomorphous series. Much discussed in the literature relation between the variability of the refractive indices and chemical composition of members of this series seems to be more influenced by the extent of Si substitution by Al ions than by the content of large cations, like K, Ba, Sr, per unit cell.

INTRODUCTION

In accordance with the most frequently reported mode of occurrence the recently examined harmotome appears in partly hydrothermally altered melanocratic basalt, known until yet as basalt (Kamieński 1931), constituting submarine effusions associated with their hyaloclastites.

Basaltic rocks were also announced by Traube (1888) as parental for two harmotome occurrences in Sudeten Mountains. However, identity with this zeolite is doubtful. For instance, such conclusion was attained by Thugutt (1947) in the case of a phillipsite found in Karkonosze Mts basalt, erroneously determined as harmotome. Another mode of harmotome provenance in recent Poland's area is genetically connected with silver-cobalt-nickel hydrothermal ore formation. The only known found place is that cited by Traube (1888) and Thugutt (1947) from Fryderyka-Juliana Mine near Miedziana Góra, in Sudeten Mountains.

The last mentioned writer, acknowledged international authority in the chemistry of zeolite defines and explains (*op. cit.*) the similarity of the chemical composition and structure of harmotome and phillipsite, as well as their provenance. For the first mineral as the most probable source he recognized K-feldspars and for the second one — nepheline. Noteworthy is also the microchemical and optical procedure elaborated by Thugutt and Woyno (1925 a, b) for fast identification of phillipsite-harmotome solid solution series minerals.

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If the amount of available material is limited the best now disponible and generally used method is based on the X-ray diffraction patterns. However, it requires high precision of measurements, to avoid possible mistakes, one of which will later be discussed. Another, seemingly obsolete but in reality simple, fast and in this case infallible procedure of distinction of Ba-rich members of phillipsite-harmotome series remains the specific gravity determination. Obtained data, likewise X-ray data, allow to estimate the approximate content of heavy and large cations.

ENVIRONMENTAL CONDITIONS OF OCCURRENCE

Available data regarding geological modes of occurrence of until now examined harmotome mineralizations let imply, independently of needed element concentrations, the importance of elevated temperature in aqueous solutions. This may be deduced from specific environmental features accompanying infilling with precipitation products of voids and fissures in the cooling volcanite, pegmatite and hydrothermal ore bodies. The following analysis of environmental conditions which dominated during the formation of here recorded harmotome (\pm pyrite) in form of linings covering walls of voids and fissures in the Biała Woda Gorge melabasalt yields another evidence of the elevated temperature significance in harmotome generation.

The voids, now amygdales filled predominantly by calcite, abound there particularly in the peripheral top parties of submarine lava flow. To the acceptance of submarine environmental conditions, besides shape and size of voids inclines co-occurrence of hyaloclastites with calcite matrix and specific type of glass and mafite crystals alteration, namely: smectitization, chloritization and carbonatization. The local concentration of volatiles, especially of water, mainly sea water assimilated from surroundings chiefly in the later stages of magma cooling, conduced to resurgent boiling. This process was responsible for the formation of voids (vesiculation) and for far-reaching transformations in their nearest vicinity. This way generated aureoles are well expressed by: 1-o — remarkable augmentation of crystal size, 2-o — retardation of glass alteration processes through its hydration, 3-o — lack of smaller microliths due to decreased viscosity forcing crystal growth but restricting nucleation, 4-o appearance of Fe^{3+} — and Ti-rich augites, lamprobolites and biotites, 5-o — concentration of phosphorus in form of apatite.

The way in which these factors agitated may be elucidated only by involving the water enrichment of magma and abundance of incompatible elements (Fe, Ti, P, a.o.) during crystallization of the last magma portions, preceding and accompanying resurgent boiling. This process taking place only at defined p-t conditions in top parties of lava body is connected with heat loss and increase of pneumatic pressure. In the same time the released vapors cause vesiculation of magma. The rised dissociation of water molecules, with connected higher oxygen fugacity, explains trivalent iron prevalence. In presence of Fe^{3+} the solubility of hydrogen (H_2) substantially increases what leads to the reversible reaction of reduction and hydrolysis, which after Burnham (1979) may be expressed as follows: $1/2 H_2 + O^{2-} + Fe^{3+} = OH^- + Fe^{2+}$. Trivalent iron ions become easily fixed in lamprobolite (oxyhornblende), biotite, and especially, in haematite crystal lattices. Similar to the described vesiculation and mineralization of aureoles phenomena were reported by Walker and Cameron (1983) from hyaline boninites from Western Pacific.

In later stages of magma cooling, after resurgent boiling, the reduction potential and alkalinity of solutions increased steadily and with them the concentration of hydrogen sulphide, manifested by precipitation of pyrite, lining void walls. Just

after iron bisulphide precipitation appeared harmotome crystals, followed later by calcite accumulations. This might, at last, be accomplished from solutions having temperature insignificantly differing or not differing that dominating in surroundings. This same calcite generation constitutes the matrix in hyaloclastites accreted to solid lava and forming together the olistolithic block.

MORPHOLOGICAL AND PHYSICAL PROPERTIES

The persistence of occurrence of the same, thick prismatic, slightly flattened habit of crystals and specific twinnings in harmotome is a commonplace often emphasized. The mentioned shape with flattening parallel to $\{010\}$ or $\{001\}$ and two kinds of twinning are own to harmotome crystals found in Biała Woda melabasalt. The size of twinned, salmon- to flesh-red grains reaches up to nearly 1 mm. in length. Noteworthy is the fact, that euhedral development of crystal boundaries, twinning sutures and combination striations can be detected on each grain; although no examples of re-entrant angles were disclosed. Judging from the values for interfacial angles, the presence of characteristic striae parallel to the edges between $\{110\}$ and $\{010\}$ (see Fig. 1b) and twin suture running parallel to $\{001\}$, the most frequent twin variety form simple, pseudo-orthorhombic penetration twins after the so-called morvenite law. Much more rarely observed are multiple pseudotetragonal twins—fourlings after Marburg law. They show (Fig. 1a) only striated faces of $\{110\}$ and $\{010\}$ simple forms and additional sutures — intersections of composition surfaces close to the $\{011\}$ simple form orientation.

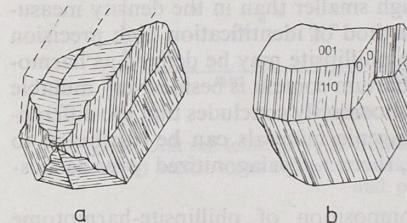


Fig. 1. Idealized image of a penetration twin, fourling of the Marburg type (a), deprived of re-entrant angles and showing pseudotetragonal symmetry. It is less common among Biała Woda harmotomes than the morvenite type penetration twin (b), of pseudo-orthorhombic symmetry

The optical properties determined using universal stage techniques, mainly on cleavage flakes parallel to $\{010\}$, may be summarized, as follows: $n_y = 1.512 - 1.513 \pm 0.001$; $n_\beta = 1.509 - 1.510$; $n_x = 1.506 - 1.507$; $n_y - n_x = 0.006 \pm 0.001$; $2V_\gamma = 84^\circ \pm 1^\circ$; $\alpha/a = 63^\circ \pm 1^\circ$.

The specific gravity of examined harmotome, measured in the mixture of benzene and bromoform, equals 2.465 ± 0.005 g/cm³. It should be here remarked that in phillipsites it amounts nearly 2.2, in barium-poor wellsites — from 2.25 to 2.37 and in barium-rich hatmotomes — from 2.41 to 2.49.

The approximate evaluation of barium content may be also obtained from X-ray diffractometric data in the form of unit cell dimensions, calculated from interplanar distances. This more quickly may be accomplished directly, taking into account only some reflections from the following listed values, selected from one of the Biała Woda harmotome samples: 1) — $d_{100,101} = 8.142$ Å (10), 2) — $d_{002,020} = 7.176$ (8), 3) — $d_{012} = 6.402$ (10), 4) — $d_{022,200} = 5.040$ (4), 5) — $d_{103} = 4.297$ (5), 6) — $d_x = 4.084$ (10)_{broad}, 7) — $d_{212,210} = 3.898$ (3), 8) — $d_{301,141} = 3.240$ (2), 9) — $d_{042_{a,o}} = 3.171$ (3), 10) — $d_{311_{a,o}} = 3.116$ (3), 11) — $d_{321} = 2.918$ (2), 12) — $d_{105,143} = 2.738$ (4), 13) — $d_x = 2.679$ (8)_{broad}, 14) — $d_{323} = 2.528$ (4).

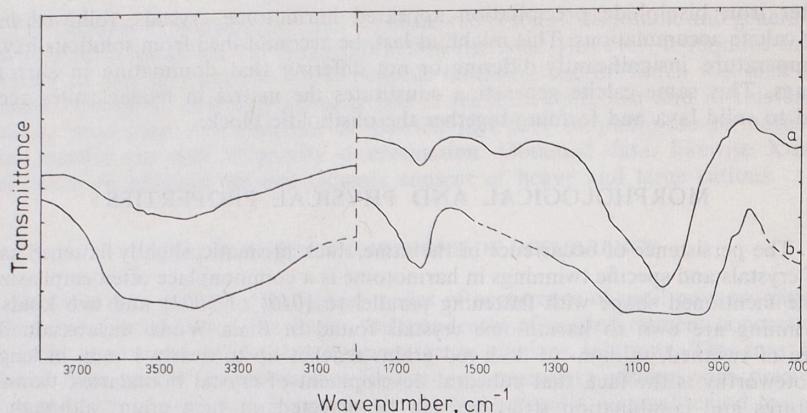


Fig. 2. Infrared absorption spectra of Biala Woda harmotome (a) and of phillipsite (b), after Harada et al. 1967. Note: dotted line in second case signifies elimination of the absorption bands due to Nujol

Specially variable and hence most indicative for distinction seem to be the following reflections: no. 7 ($d = 3.87-3.91 \text{ \AA}$ in harmotome and $3.94-3.98$ in phillipsite), no. 11 (2.88—2.92 and 2.93—2.95, respectively), no. 12 (2.71—2.73 and 2.74—2.76, resp.), no. 14 (2.51—2.528 and 2.534—2.548, resp. while in wellsite = 2.531), as well as low intensity of the reflection no. 1 in phillipsite. The degree of confidence resulting from this deduction is sufficient, though smaller than in the density measurements case. Therefore, in described X-ray method of identification high precision is absolutely needed; otherwise barium-bearing phillipsite may be defined as harmotome, as was done by Morgenstern (1967). The barium content is besides very mutable from sample to sample. Lately mentioned author correctly concludes that the difference in the Ba content in phillipsite group authigenic minerals can be attributed to the difference in the composition of parental, there — palagonitized pyroclastics-rich marine sediments.

Some indication concerning chemical composition of phillipsite-harmotome isomorphous series offer, moreover, infrared absorption spectra. This is illustrated on the spectrogram (Fig. 2) when comparing spectra for Biala Woda harmotome (a) and phillipsite (b), reproduced from Harada et al. (1967) work. The band at 1040 cm^{-1} in harmotome is much better defined than enlarged one in phillipsite. They, according to Milkey (1960), may develop due to the primarily bond-stretching vibrations of the O—Si—O linkages. He also presumes that the substitution of Al, which has a smaller mass than Si, would result in higher frequency. Moreover, Harada et al. (1967) emphasized the spreading toward higher frequencies of absorption band at 3400 cm^{-1} in the water-stretching region.

To the most discussed in literature problems regarding constitution and its variability of phillipsite group minerals appertains the dependence between the refractive indices variation and chemical constitution. Hay (1964) found that the index of refraction of phillipsites decreases with an increase in the Si/Al ratio. For example, phillipsites having Si/Al ratio less than 2 usually show R.I. oscillating between 1.48—1.51, whereas those with Si/Al amounting 3 and more — R.I. of 1.44—1.48. This inference was called into question after Sheppard and Gude (1970) investigations of deep-sea authigenic phillipsites. These authors tried without success to correlate the R.I. with Si/Al ratio. However, they suggest that R.I. seem to be

affected by the Ba and Na contents. Galli and Loschi Ghittoni (1972) attempted to make a revision of the last conclusion by correlating n_{γ} , n_{β} , and n_{α} as well as mean R.I. with weight per cent of BaO and Na₂O without positive result.

Present author constructed diagram demonstrating the relation between mean R.I. values and Al and K contents per unit cells comprising 32 oxygen atoms (Fig. 3) Plotted available data for phillipsite-harmotome series members with few exceptions reveal rather well expressed trend in distribution of projection points. This argues the correctness of formerly implied influence of Si—Al substitution on the refractive indices values. Much less marked is the dependence of these values with changing potassium contents.

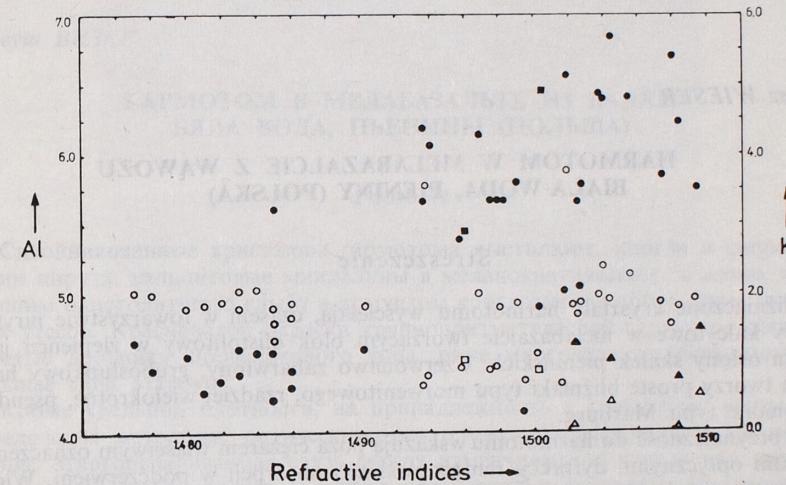


Fig. 3. Unit cell (embracing 32 oxygen ions) contents of Al (filled symbols) and K (open symbols) versus mean refractive indices in harmotomes (triangles), wellsites (squares) and phillipsites (circles)

The significance of other element contents as deciding factors for refractivity power, as of sodium and barium is still disputable. Another element contents were even not considered, though such as strontium, calcium, iron a.o. may appear in noticeable amounts. It should be pointed out that emission-spectral, semiquantitative analysis of Biala Woda harmotome disclosed the presence of 0.1 per cent of Sr, 0.1 per cent of Fe, 0.5 per cent of Mg and 3.0 per cent of Ca.

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HARMOTOM W MELABAZALCIE Z WĄWOZU BIAŁA WODA, PIENINY (POLSKA)

Streszczenie

Zbliżniaczone kryształy harmotomu wyścielają, czasem w towarzystwie pirytu, migdały kalcytowe w melabazalcie tworzącym blok olistolitowy w zlepieńcu jarmuckim osłony skałek pienińskich. Czerwonawo zabarwiony, grubosłupkowy harmotom tworzy proste bliźniaki typu morwenitowego, rzadziej wielokrotne, pseudo-tetragonalne typu Marburg.

Na przynależność do harmotomu wskazują poza ciężarem właściwym oznaczenia metodami optycznymi, dyfrakcji rentgenowskiej i absorpcji w podcerwieni. Wiele dyskutowanych związków między zmiennością współczynnika załamania światła i składem chemicznym członów szeregu roztworów stałych filipsyt—harmotom wydaje się być bardziej uzależnionej od stopnia substytucji jonów Si przez Al aniżeli od zawartości dużych lub/i ciężkich kationów, jak K czy Ba.

Powstaniu harmotomu sprzyja podwyższona temperatura roztworów wzbożyczych w tzw. niezgodne pierwiastki (K, Ba, P i in.), pozostałe po wrzeniu resurgentnym. Ten ostatni proces nie tylko spowodował znaczne przeobrażenia w stropowych częściach podmorskiego, w danym przypadku potoku lawowego, ale i intensywne pęcherzykowanie. Wakuole ostatecznie zapieśniły kalcyt tej samej generacji co i tworzący spojwo w hyaloklastytach, współwystępujących z lawą melabazaltową.

OBJAŚNIENIA FIGUR

- Fig. 1. Idealizowany obraz bliźniaka penetracyjnego, czwóraka typu Marburg (a), pozbawionego kątów wkleśnych i wykazującego symetrię pseudotetragonalną. Jest on mniej pospolity wśród harmotomów z Białej Wody aniżeli typ morwenitowy bliźniaków (b) o pseudorombowej symetrii.
- Fig. 2. Widma absorpcyjne w podcerwieni harmotomu z Białej Wody (a) i filipsytu (b), za Haradą i in. 1967. Uwaga: linia przerywana w drugim przypadku oznacza usunięcie pasm absorpcyjnych z powodu nujolu.
- Fig. 3. Zawartości Al (pełne symbole) i K (puste symbole) w komórkach jednostkowych (obejmujących 32 jony tlenu) względem współczynników załamania harmotomów (trójkąty), wellsytów (kwadraty) i filipsytów (koła).

OBJAŚNIENIA FOTOGRAFII

- Fot. 1. Grupa bliźniaków harmotomu wyseparowana z pęcherzyka wypełnionego kalcytem. Jedno ze zbliżniaczych (wg prawa Marburg) ziarn ukazuje lśniącą ścianę (110), złożoną z dwóch subindywiduów. Pow. \times 37. Porównaj fig. 1a
- Fot. 2. Orientowany, schodkowy narost na zbliżniaczonym (wg prawa morwenitowego) krysztale harmotomu, częściowo wyizolowanego z kalcytowego migdału. Pow. \times 37
- Fot. 3. Przekrój (płytki cienka) melabazaltu z wawozu Białej Wody z pęcherzykiem wyścielonym euhedralnym harmotomem (czarny w świetle przy skrzyżowanych nikolach) i wypełnionym kalcytem. Pow. \times 70

Тадеуш ВИЗЕР

ГАРМОТОМ В МЕЛАБАЗАЛЬТЕ ИЗ БАЛКИ БЯЛА ВОДА, ПЬЕНИНЫ (ПОЛЬША)

Резюме

Сдвойниковые кристаллы гармотома выстилают, иногда в сопровождении пирита, кальцитовые миндалины в меланократическом базальте, образующим олистолитовую глыбу в ярмуцком конгломерате обрамления пьенинских утесов. Красноватой окраски крупнопризматический гармотом образует простые двойники морвенитового типа, реже многократные псевдотетрагональные типа Марбург.

Кроме удельной плотности, на принадлежность к гармотому указывают определения методами: оптическим, рентгеновской дифракции и ИК-поглощения. Многооспариваемая связь между изменчивостью показателя преломления и химическим составом членов ряда твердых растворов филлипсит — гармотом кажется более зависимой от степени замещения ионов Si ионами Al, чем содержанием крупных и (или) тяжелых катионов, как K либо Ba.

Образованию гармотома содействует повышенная температура растворов, обогащенных в так называемые несогласные элементы (K, Ba, P и др.), остающиеся после резургентного кипения. Этот последний процесс не только вызвал значительные преобразования в кровельных частях подморского, в данном случае лавового потока, но и интенсивное образование пузырей. Вакуоли в конечном итоге заполнили этой же самой генерации кальцит, что и образующий цемент в гиалокластитах, сопутствующих мелабазальтовой лаве.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Идеализированная картина пенетративного четверного двойника типа Марбург (a), лишенного вогнутых углов и обнаруживающего псевдотетрагональную симметрию. Среди гармотомов из Бялой Воды он менее распространен, чем морвенитовый тип двойников (b) псевдоромбической симметрии.
- Фиг. 2. ИК-спектры поглощения гармотома из Бялой Воды (a) и филлипсита (b), по Хараде и др. 1967. Примечание: прерывистая линия во втором случае обозначает удаление полос поглощения из-за парафинового масла.
- Фиг. 3. Содержания Al (полные символы) и K (пустые символы) в элементарных ячейках (32 иона кислорода) по отношению к коэффициентам преломления гармотомов (треугольники), уэллситов (квадраты) и филлипситов (кружки).

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

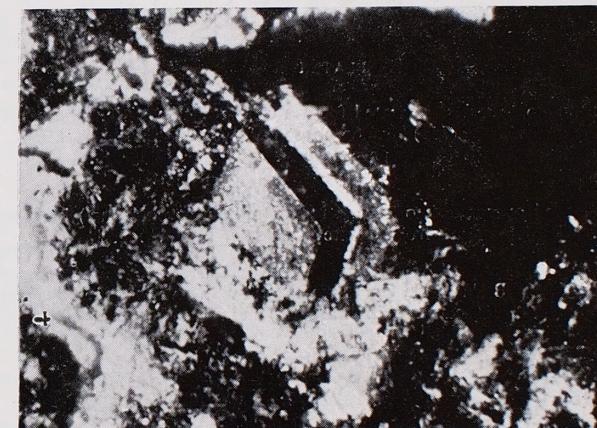
- Фото 1. Группа двойников гармотома, выделенная из пузыря выполненного кальцитом. Одно из сдвойниковых зерен (по закону Марбург) обнаруживает блестящую грань {110}, сложенную из двух субиндивидов. Увел. $\times 37$. Сравни фиг. 1а
- Фото 2. Ориентированный ступенчатый нарост на сдвойникованном (по морвенитовому закону) кристалле гармотома, частично выделенному из кальцитовой миндалины. Увел. $\times 37$
- Фото 3. Разрез (прозрачный шлиф) мелабазальта из балки Бяла Вода с пузырем, выстеленным идиоморфным гармотомом (черный, в скрещенных николах) и выполненным кальцитом. Увел. $\times 70$

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PLATE I



Phot. 1



Phot. 2



Phot. 3

Tadeusz WIESER — Harmotome in melabasalt from Biala Woda Gorge, Pieniny Mountains (Poland)

PLATE I

Phot. 1. Group of harmotome twins separated from a calcite-filled vesicle. One of twinned (after Marburg law) grains shows shining (110) face, composed of two subindividuals. Magn. $\times 37$. Compare Fig. 1a

Phot. 2. Oriented, stepped overgrowth on the twinned (after morvenite law) harmotome crystal, partly isolated from calcite amygdale. Magn. $\times 37$

Phot. 3. Section (thin slide) of Biała Woda Gorge melabasalt with a vesicle lined by euhedral harmotome (black under crossed nicols illumination) and filled by calcite. Magn. $\times 70$