

Marek MUSZYŃSKI<sup>1</sup>, Piotr WYSZOMIRSKI<sup>2</sup>

### HARMOTOME FROM A NEW OCCURRENCE OF RED BEDS IN THE UPPER SILESIA COAL BASIN (POLAND)

**Abstract.** Harmotome has been identified, using optical microscopy, XRD, IR, SEM/EDS and DTA, in an altered collapse breccia in a new occurrence of the so-called red beds in the Upper Silesian Coal Basin ("Marcel" mine). The mineral occurs in some metasomatized clasts, in the breccia matrix and in some microdruses and sealed vugs. Prismatic, subhedral crystals of harmotome present in the druses are most often transparent and colourless and reach a length of 0.5 mm. In most cases, they form penetration twins with pseudo-tetragonal (morvenite type) and pseudo-orthorhombic (Marburg type) symmetry. The chemical formulae of two crystals analysed using EDS are as follows:



The harmotome originated at a last stage in the evolution of the red beds; their younger component, dioctahedral smectite, occurs only locally. The harmotome could have formed as a result of either supergene weathering of Carboniferous rocks (previously thermally altered by coal fires) or during later diagenesis of the products of these alterations when the Carboniferous strata were buried under Miocene sediments. Barium was contained in sulphate-free or sulphate-poor pore waters in the Carboniferous rocks of the coal basin.

*Key-words:* harmotome, red beds, Upper Silesian Coal Basin, Poland

### INTRODUCTION

Harmotome is known from a few places only in Poland. In the second half of the 19<sup>th</sup> century, it was described from two localities in Lower Silesia: the Miedzianka–Ciechanowice area (German *Kupferberg–Rudelstadt*) near Janowice Wielkie (*Jannowitz*) by Websky and Traube, and Mrowieniec (*Finkenhubel*) near Kłodzko (*Glatz*) by Websky, Coleman and Traube (*vide* Lis, Sylwestrzak 1986). In the Miedzianka–Ciechanowice

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<sup>1</sup> AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Kraków, Poland

<sup>2</sup> AGH University of Science and Technology, Faculty of Material Science and Ceramics, al. Mickiewicza 30, 30-059 Kraków, Poland

area, the harmotome occurs in hydrothermal barite-calcite veins containing Ag, Co and Ni ore minerals and in barren calcite veins. In Mrowieniec, it occurs associated with quartz and goethite in geodes in loose melaphyre blocks. Kowalski (1977, 1981) reported harmotome in the so-called red beds of the Upper Silesian Coal Basin (USCB) in the Rybnik area, where it occurs in the “Jastrzębie”, “Moszczenica” and “Knurów” coal mines. The mineral occurs as microdruses in fractures and vugs. It also forms veins and replaces older assemblages in the altered Carboniferous rocks. The accompanying minerals include analcite, phillipsite, natrolite, smectite, hematite, hydrohematite, maghemite, quartz, gibbsite, hydrohalloysite, kaolinite and chlorite. It merits noting that in analogous red beds in the Czech part of the USCB, harmotome was described by Králík (1971, 1982). Lastly, Wieser (1985) described harmotome from amygdales in a basalt olivolith from the Biała Woda gorge in the Pieniny Clippen Belt where it is associated with calcite and pyrite.

In this paper, harmotome from a new occurrence in the “Marcel” coal mine in the southern part of the Chwałowice trough (Lipiarski et al. 2004 — Fig. 1A) is described. There, zeolite-bearing red beds similar to those described by Kowalski (1977, 1981) and Králík (1971, 1982) were exposed in 2001.

Our laboratory investigations involved besides optical microscopy also X-ray diffraction (Philips X Pert APD diffractometer), thermal analysis (Hungarian MOM Derivatograph-C), infrared absorption spectroscopy (BIO-RAD FTIR 165 spectrometer with samples as KBr tablets) and scanning electron microscopy combined with chemical microanalysis (HITACHI S-4700 microscope coupled to a NORAN Vantage spectrometer). Samples analysed using SEM/EDS were covered with carbon and chemical EDS determinations were carried out using the spot method. Most of the investigations were made on harmotome crystals separated manually under a stereoscopic microscope.

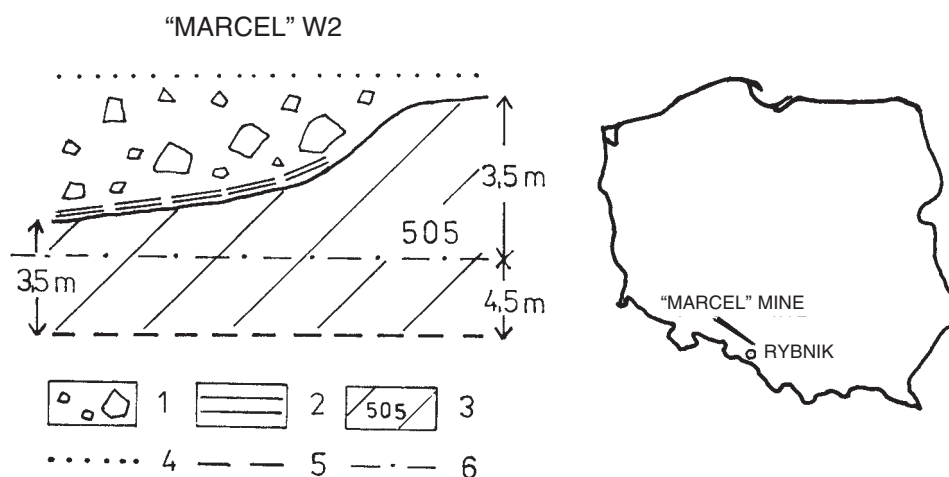


Fig. 1. Sketch (not to scale) of the W2 exposure (a cross-cut at the 300 m level) in red beds of the “Marcel” mine

1 — collapse breccia containing harmotome, 2 — alunite claystone, 3 — coal — seam No. 505, 4 — roof of the cross-cut, 5 — bottom of seam No. 505 tapped with boreholes, 6 — bottom of the cross-cut

## GENERAL CHARACTERISTICS OF THE ALTERED COLLAPSE BRECCIA CONTAINING HARMOTOME

The harmotome was found in strongly altered collapse breccia that is almost the sole component of the red beds exposed in the "Marcel" mine (Fig. 1). Only in places is the breccia seen to be separated from a fragment of the preserved coal seam by a thin (up to 0.5 mm), discontinuous layer of light rusty-beige alunite claystone (Lipiarski et al. 2004). This claystone is essentially composed of smectite, illite and alunite accompanied by minor hematite and traces of quartz.

The breccia clasts range in size from a fraction of a millimetre to over 50 centimetres. They are irregular and diversified in shape and represent Carboniferous claystones and subordinate mudstones thermally altered by coal fires, in places even vitrified. They were also metasomatized. Their mineral composition varies depending on the composition of the parent rocks and the intensity of the alterations. The prevalent minerals of the clasts most often include smectite along with minerals of the kaolinite group (halloysite  $-10\text{\AA}$  and  $-7\text{\AA}$  and probably kaolinite-D) and detrital quartz accompanied, in rare instances, by neogenic microcrystalline quartz. Harmotome, hematite, cristobalite, tridymite, mullite, calcite and siderite, coal matter (in some clasts), illite and/or mixed-layer illite/smectite are minor components.

The binding mass of the breccia comprises a non-homogenous mixture of smectite, quartz, hematite, harmotome, kaolinite group minerals, goethite, mullite, siderite and traces of alunite, chalcopyrite and sphalerite.

Common fractures, and vugs up to 2–3 mm in diameter that resemble vesicles in volcanic rocks, are partly or completely filled with smectite, harmotome, siderite, kaolinite group minerals, cristobalite, hematite, goethite, siderite and, in some instances, quartz.

## RESULTS OF INVESTIGATIONS ON HARMOTOME

Harmotome is generally a minor component of the collapse breccia. Its distribution is, however, very irregular, varying from almost nil in places to abundant local concentrations comprising up to 75 wt.% of the rock — as estimated from DTA (Fig. 2) and XRD analyses. The richest in harmotome are some fine-blastic clasts, probably derived from feldspar-rich mudstones, and some porous fragments in the breccia matrix. Harmotome also concentrates in some veins, on fracture walls and in vugs (vesicles). In the clasts, this zeolite is crypto- and microcrystalline and, as a result, can only be identified by X-ray diffraction. The harmotome sealing fractures and other vugs, and sometimes forming microdruses, occurs as larger, prismatic, tabular or acicular, subhedral crystals (Figs 3–12; 13A, B). These, ranging up to 0.5 mm of length, show variable elongation, usually below 1:4 (maximum 1:14). Most often, they do not occur as single crystals but form random, parallel, radial or spherulithic aggregates (Figs 5–10; 13A, B) up to about 2 mm in size. Optical and SEM observations of the harmotome crystal habit, and comparison with the data of Tröger (1959), Wieser (1985), Gottardi

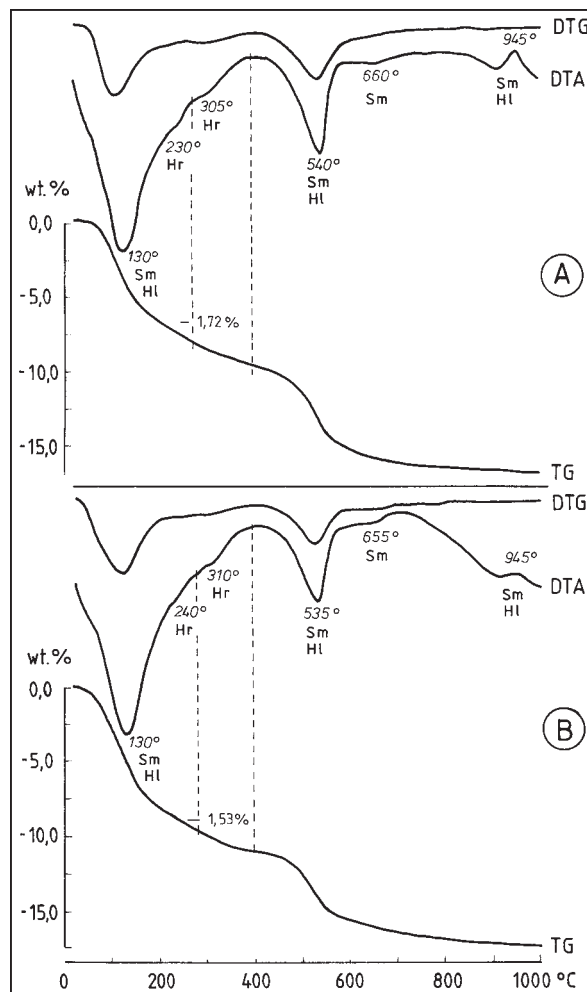


Fig. 2. DTA curves of the altered parts of the collapse breccia from red beds of the "Marcel" mine that are the richest in harmotome

A — variegated, white-cream-pale greenish clast; B — microporous, slag-like, grey-brownish matrix.

Symbols for mineral phases deemed to show thermal effects (identification supported by X-ray data):

Hr — harmotome, Hl — halloysite, Sm — smectite

and Galli (1985), indicate that the mineral prevalently forms penetration twins with pseudo-tetragonal symmetry and without re-entrant angles (comp. Figs 3–6; 13A, B with Figs 14A-b). Almost equally common are penetration twins with pseudo-orthorhombic symmetry (comp. Figs 7; 13A, B with Figs 14A-a). The pseudo-tetragonal twins are classified in older papers and according to the nomenclature of Lacroix (*vide* Sahama, Lehtinen 1967), as "morvenite type", the pseudo-orthorhombic twins as "Marburg type" (e.g., Sahama, Lehtinen 1967; Black 1969; Wieser 1985). Crystals of harmotome with a monoclinic habit, probably untwinned, are less common [comp. Figs 13A, B with Fig. 14B and Russel (1946) — Fig. 22], while cruciform-twinned intergrowths

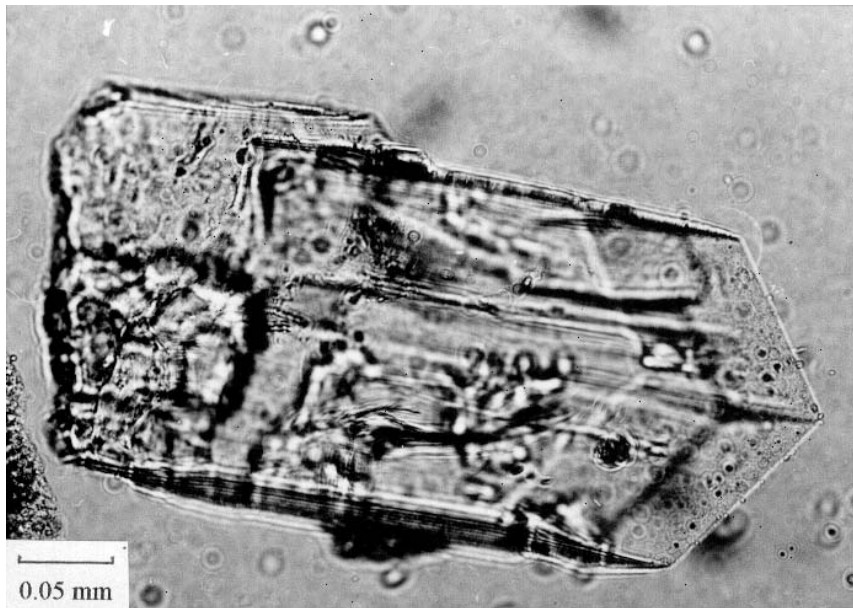


Fig. 3. Euhedral, prismatic harmotome crystal. Red beds of the "Marcel" mine. Grain mount; polarizing microscope; one polar

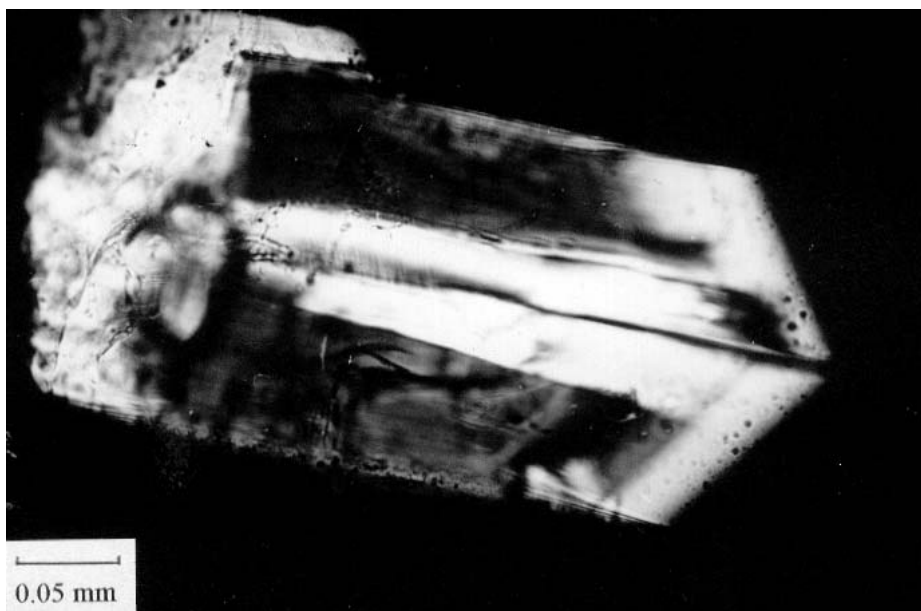


Fig. 4. *Ditto*; optical heterogeneity resulting from complex twinning is visible. Red beds of the "Marcel" mine. Grain mount; polarizing microscope; crossed polars

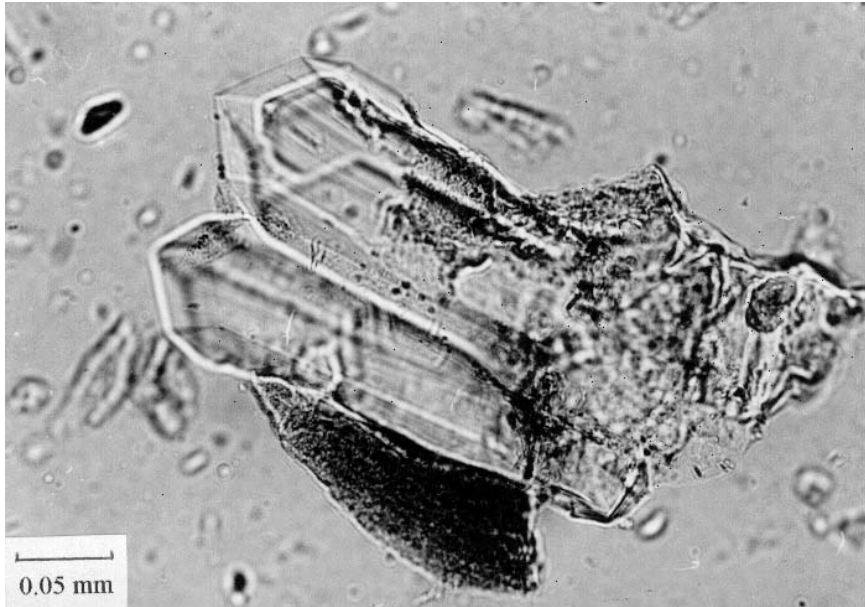


Fig. 5. Parallel intergrowth of euhedral, prismatic crystals of harmotome. Red beds of the "Marcel" mine. Grain mount; polarizing microscope; one polar

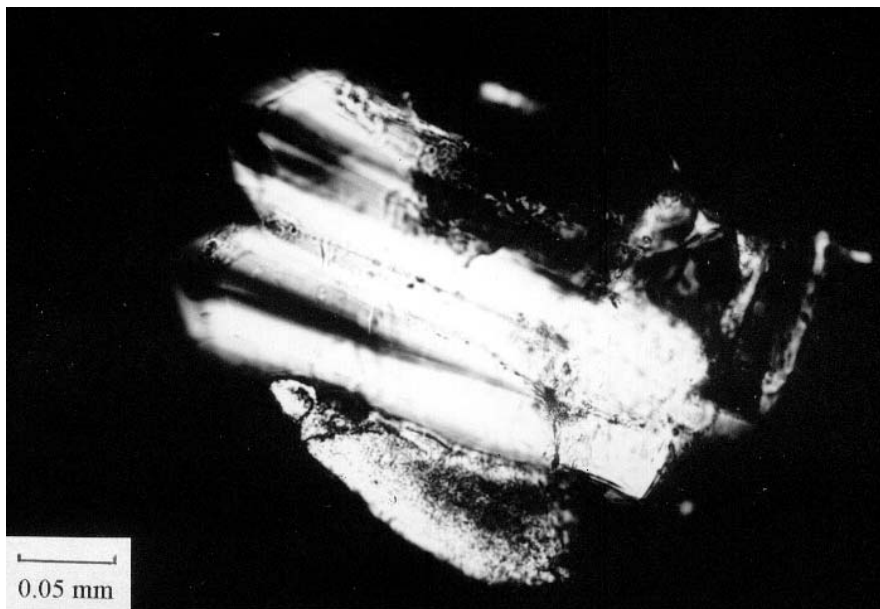


Fig. 6. *Ditto*; optical heterogeneity resulting from complex twinning is visible. Red beds of the "Marcel" mine. Grain mount; polarizing microscope; crossed polars



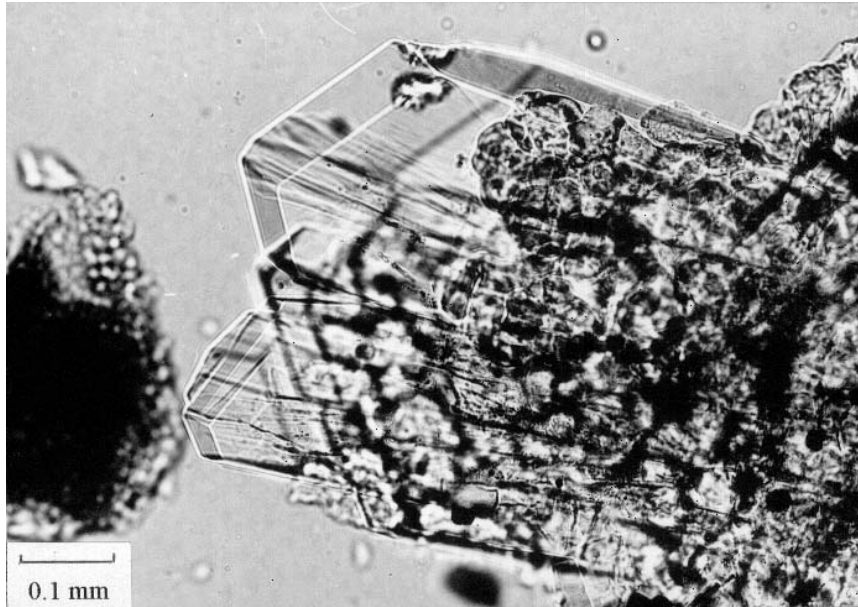


Fig. 7. Parallel intergrowth of subhedral, tabular crystals of harmotome with intergrown smectite aggregates in the lower part. Red beds of the "Marcel" mine. Grain mount; polarizing microscope; one polar

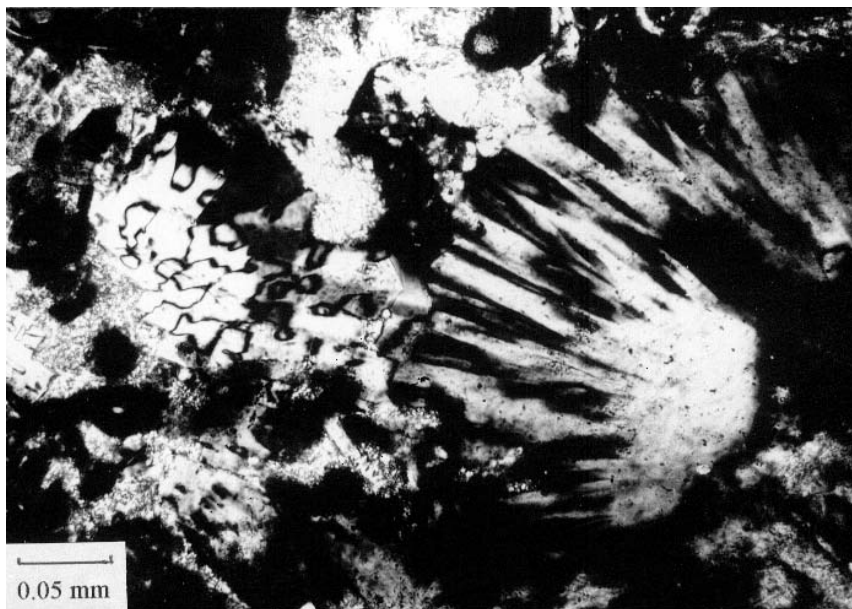


Fig. 8. Divergent-radial aggregate of acicular crystals of harmotome. Red beds of the "Marcel" mine. Thin section, crossed polars



Fig. 9. Fragment of a spherulitic aggregate of acicular crystals of harmotome intergrown with smectite (black parts). Red beds of the "Marcel" mine. Grain mount; polarizing microscope; one polar

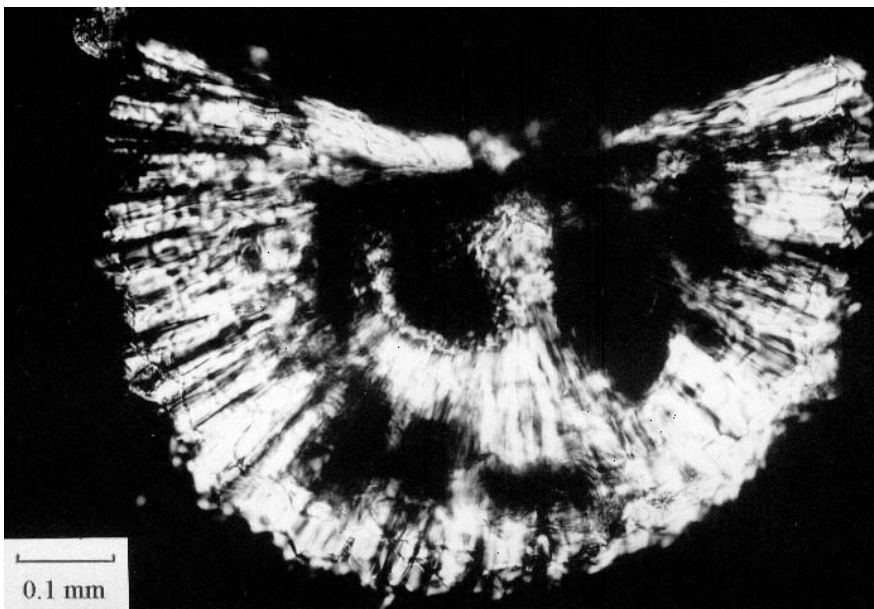


Fig. 10. *Ditto*; crossed polars



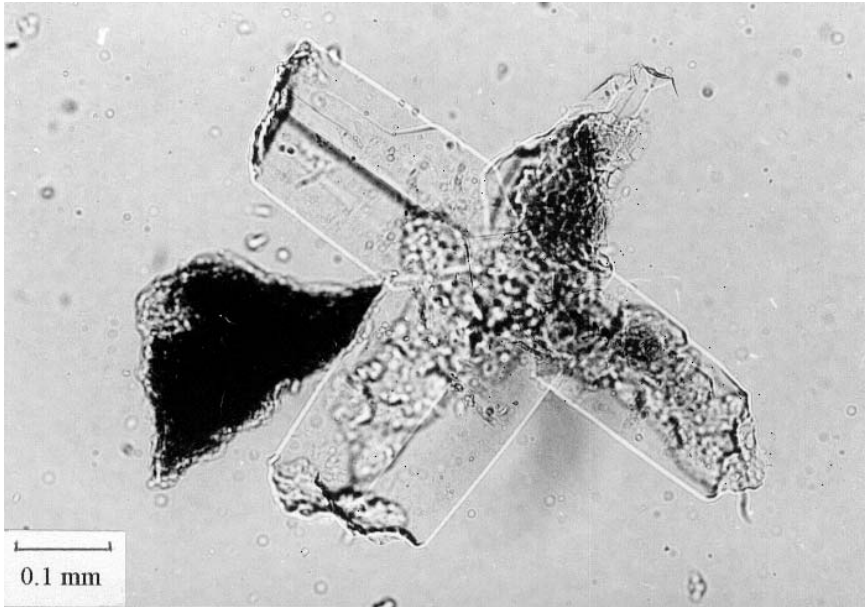


Fig. 11. Cross-like intergrowth of prismatic, partly broken crystals of harmotome. Red beds of the "Marcel" mine. Grain mount; polarizing microscope; one polar

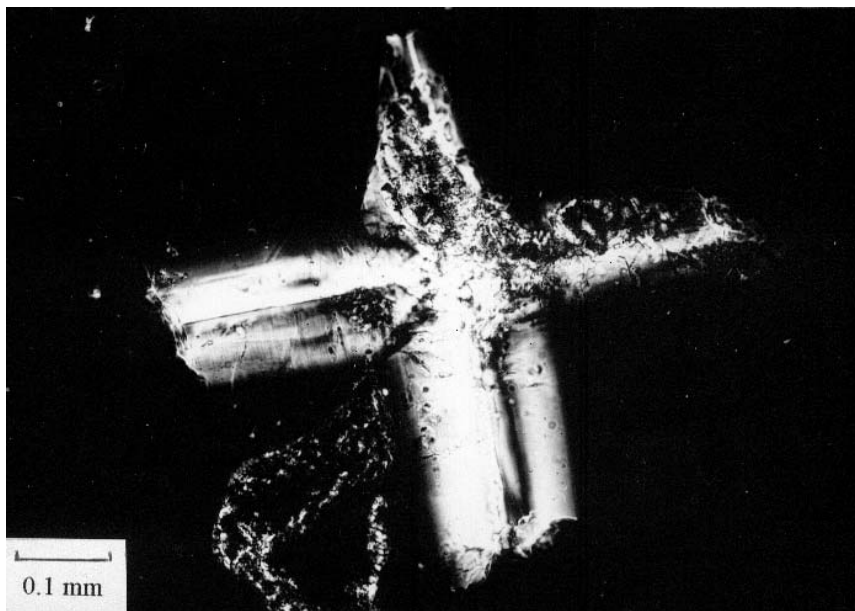


Fig. 12. *Ditto*; crossed polars

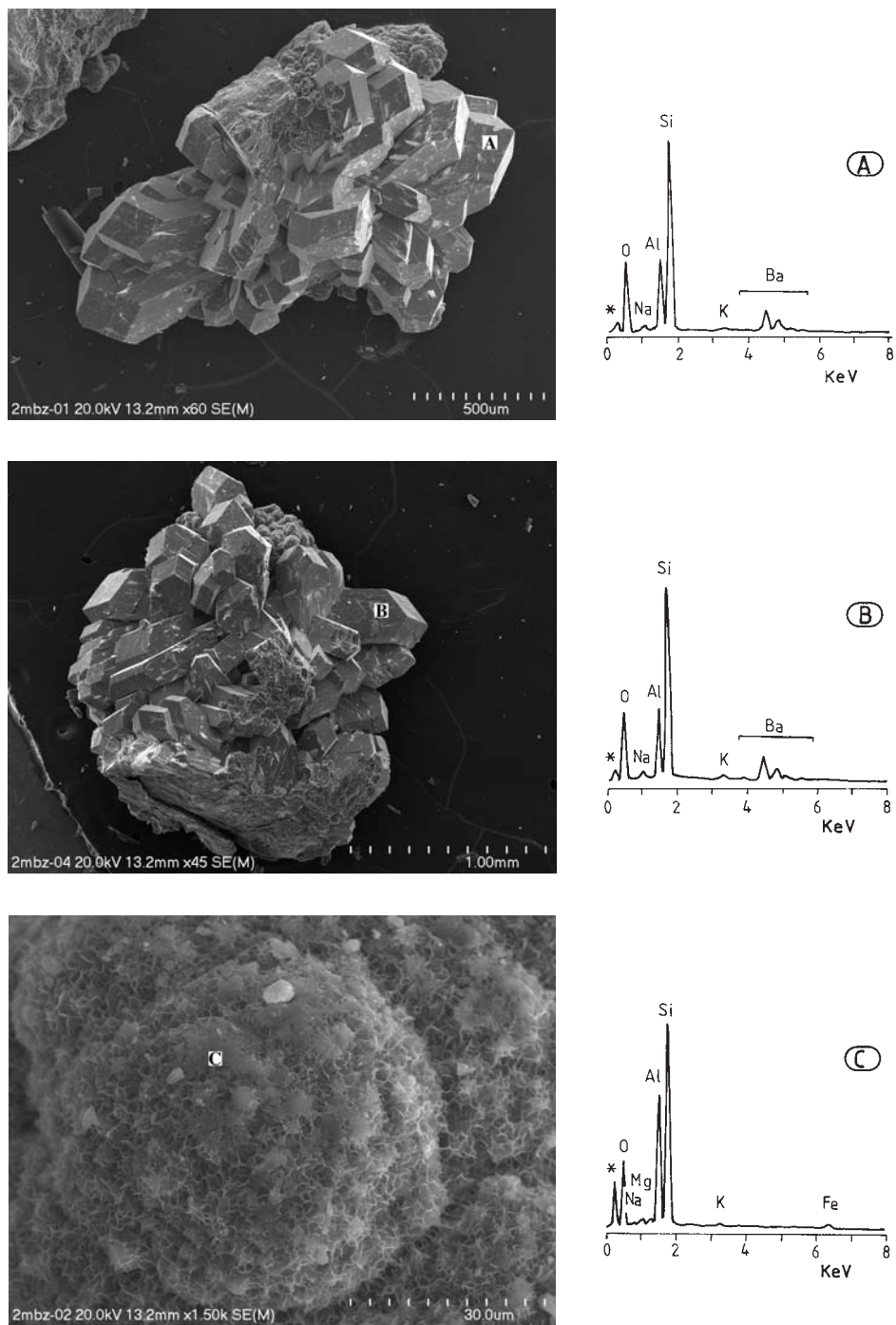


Fig. 13. SEM/EDS analyses: A, B — crystals of harmotome from microaggregates (see also Table 2);  
 C — smectite overgrowing a crystal of harmotome. Red beds of the "Marcel" mine.

\* — line of carbon used in covering the surface of the sample

(Figs 11, 12) are rare. The lack of striation on the faces of the harmotome crystals is remarkable as others often report its presence (e.g., Deer et al. 1963; Sahama, Lehtinen 1967; Akizuki 1985; Wieser 1985). Complex twinning of the harmotome typically results in a characteristic uneven extinction under crossed polars (Figs 4, 6, 12). The harmotome is transparent or translucent with a vitreous lustre, and though crystals are typically colourless, some fragments may be pink, yellow-brownish or pale beige.

The harmotome crystals overgrow various minerals in the red beds. They are overgrown by and, occasionally, intergrown with a younger, dioctahedral smectite (Lipiarski et al. — in preparation) occurring as microaggregates (Figs 7, 9, 10, 13C).

The X-ray patterns of the harmotome correspond well with the reference data, particularly the comprehensive data of Gottardi and Galli (1985) for the Andreasberg (Germany) harmotome (Table 1). Reflections with the  $d_{hkl}$  values 5.35; 4.97 and 3.222 Å also pertain to the harmotome studied; they appear in other XRD harmotome data (ICDD 25-855; Sheppard, Gude 1983) and are also present in the X-ray patterns of welsite and phillipsite, two minerals isostructural with harmotome (Gottardi, Galli 1985; Franus 1999).

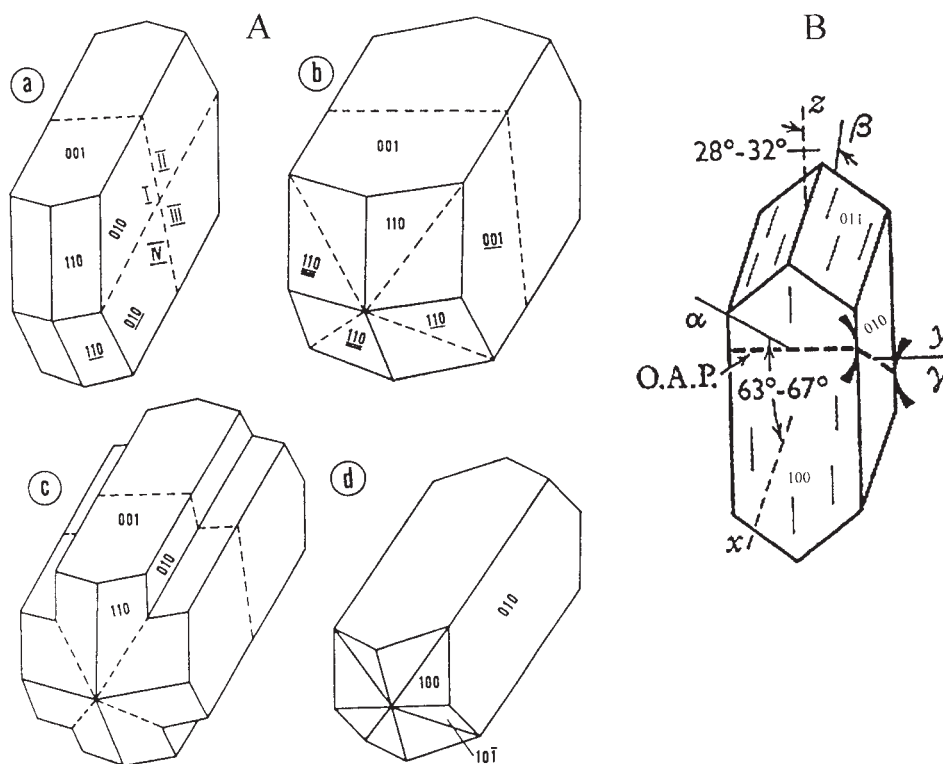


Fig. 14. Harmotome crystal habits:  
 A — after Gottardi, Galli (1985) (a — fourling, b — prismatic eightling, c — cross-shaped eightling,  
 d — less frequent type of fourling; for details see paper cited);  
 B — after Deer et al. (1963)

TABLE 1

XRD data of harmotome from red beds of the „Marcel” mine

Harmotome: „Marcel” mine		Harmotome: Andreasberg, Germany (Gottardi, Galli 1985) ICDD 39-1377		
d(Å)	I	d(Å)	I	hkl*
8.18	45	8.12	60	10-1
7.17	62	7.16	65	001
—	—	7.05	19	110, 11-1
6.39	77	6.39	95	011
5.35**	2**	—	—	—
5.04	35	5.03	32	021
4.97**	2**	—	—	—
4.30	27	4.31	33	101
		4.30	35	10-2
4.11	42	4.11	56	111, 11-2
4.09	54	4.07	67	13-1
4.07	36	4.05	59	22-1
3.914	14	3.895	32	21-2
3.671	3	3.667	10	12-2
3.571	5	3.573	5	002
3.542	7	3.528	10	040
3.467	12	3.466	18	012
3.422	2	3.410	5	23-1
3.244	46	3.241	62	14-1
3.222**	19**	—	—	—
3.191	35	3.195	28	022
3.173	55	3.169	70	041
3.143	100	3.126	100	31-2
3.085	15	3.075	31	230, 23-2
2.927	20	2.918	29	32-2
2.905	5	2.897	13	20-3
2.846	8	2.847	10	032
2.746	18	2.747	27	10-3
2.734	28	2.730	54	141, 14-2
2.696	41	2.697	61	112, 11-3
2.674	53	2.678	54	22-3
		2.671	64	150, 15-1
2.637	11	2.628	15	051
2.561	8	2.561	9	12-3
2.532	11	2.529	33	32-3
2.518	9	2.515	20	042
2.471	7	2.470	11	40-2
2.462	3	2.464	11	23-3
2.376	11	2.369	18	13-3
2.359	8	2.343	15	33-3, 40-1
2.327	14	2.320	23	250, 25-2
2.311	8	2.299	10	41-3
2.264	4	2.261	10	160, 023
2.242	11	2.241	15	241, 24-3
2.157	8	2.151	18	340, 34-3

\* The hkl values given are only those that among the values of Gottardi and Galli (1985, also in ICDD 39-1377) correspond to monoclinic structure of harmotome (see also Coombs et al. 1997).

\*\* Reflections attributed to harmotome; they appear in other XRD patterns of harmotome (ICDD 25-855; Sheppard, Gude 1983), and also are present in X-ray patterns of welsite and phillipsite, minerals isostructural with harmotome (Gottardi, Galli 1985; Franus 1999).

As the sample separates contain only subordinate admixtures of quartz (sample 1) and of kaolinite-group minerals (sample 2), infrared absorption analyses provided an almost full set of the absorption bands characteristic of harmotome in the selected range of wave numbers (Fig. 15). In the light of literature data that are unfortunately scarce and differing, particularly in the range 400–900  $\text{cm}^{-1}$  (comp. Moenke 1962; Pechar, Rykl 1985; Stuckenschmidt et al. 1988), the harmotome studied can be ascribed the following bands for sample 1/sample 2: 438/436; 461/467; 619/617; 696/690; 720/740, probably 797 (the band coincides with the quartz band)/795; 1035/1036; 1160/1155; 1400?; 1458?/1430; 1638/1636; 3254/3254; 3448/3448; 3621/3621  $\text{cm}^{-1}$ . According to the data of Pechar and Rykl (1985), supplemented by Stuckenschmidt et al. (1988), broad bands with maxima about 3254/3254; 3448/3448 and 3621/3621  $\text{cm}^{-1}$  should be attributed to stretching vibrations of the hydroxyl groups (H-O-H) and the bands 1638/1636  $\text{cm}^{-1}$  to bending vibrations of these groups. Vibrations of water molecules can be responsible for some bands between 600 and 800  $\text{cm}^{-1}$  (probably 619/617 and 795  $\text{cm}^{-1}$ ). The strong 1035/1036 and 1160/1155  $\text{cm}^{-1}$  bands result from stretching  $\nu_3$  (Si,Al)-O vibrations of the (Si,Al) $\text{O}_4$  tetrahedra. Absorption bands from bending (Si,Al)-O vibrations are situated in the range about 435–470  $\text{cm}^{-1}$ , whereas those from deformational (Si,Al)-O vibrations inside the tetrahedra lie in the range 690–740  $\text{cm}^{-1}$ . Very weak bands between 1400 and 1460  $\text{cm}^{-1}$  can be attributed to external vibrations of the (Si,Al) $\text{O}_4$  tetrahedra.

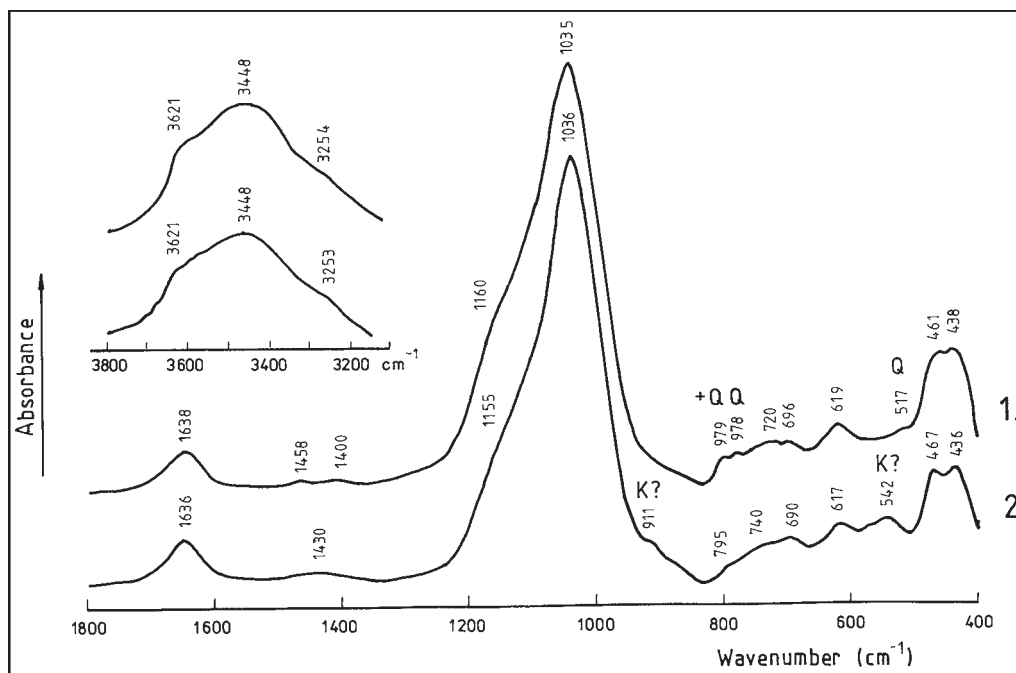


Fig. 15. Infrared absorption spectra of harmotome crystals separated from two microdruses in the red beds of the "Marcel" mine

Bands related to admixtures: K? — probably minerals of the kaolinite group, Q — quartz  
 (+ — the band coinciding with a weak absorption band of harmotome)



TABLE 2

Chemical composition of harmotomes ("Marcel" samples — EDS method, others — classical methods)

Component	"Marcel" coal mine*		1**	1'	2**	3	3'	4	5	6	7	8
	crystal A	crystal B										
SiO <sub>2</sub>			45.51	46.15	44.62	47.31	47.53	44.42	45.21	47.22	46.67	46.3
Al <sub>2</sub> O <sub>3</sub>			16.50	16.03	17.49	15.57	15.93	16.95	15.26	16.52	16.35	16.4
BaO			19.89	20.17	18.85	18.24	18.66	21.16	20.66	16.44	20.35	18.8
SrO			—	—	—	0.02	0.02	—	—	n.d.	—	n.d.
CaO			0.12	0.13	0.30	0.54	0.55	—	0.09	0.70	1.78	0.1
MnO			—	—	—	—	—	—	0.01	—	—	—
K <sub>2</sub> O			1.77	1.81	1.13	1.40	1.43	0.27	0.24	0.77	0.23	0.2
Na <sub>2</sub> O			1.18	1.21	2.49	0.53	0.54	1.59	1.81	2.22	—	1.9
Fe <sub>2</sub> O <sub>3</sub>			—	—	—	—	—	—	0.74	tr.	—	n.d.
FeO			—	—	—	0.52	—	—	—	—	—	—
MgO			0.27	—	—	0.42	—	—	0.48	—	—	0.5
H <sub>2</sub> O <sup>-</sup>			—	—	—	4.61	4.37	—	0.27	0.60	—	—
H <sub>2</sub> O <sup>+</sup>			—	—	—	10.86	10.97	—	15.57	14.92	—	—
H <sub>2</sub> O			14.74 <sup>1</sup>	14.50	14.64	—	—	15.06	—	—	14.66	(15.8)
Total			99.98	100.00	99.52	100.02	100.00	99.45	100.34	99.39	100.04	100.0
Weight % — analyses computed to 100% without H <sub>2</sub> O												
SiO <sub>2</sub>	59.47	59.71	53.39	53.97	52.57	55.95	56.14	52.64	53.50	56.30	54.67	55.0
Al <sub>2</sub> O <sub>3</sub>	18.88	18.53	19.36	18.75	20.61	18.42	18.82	20.09	18.06	19.70	19.15	19.5
BaO	18.45	18.77	23.33	23.59	22.21	21.56	22.04	25.07	24.45	19.60	23.83	22.3
SrO	—	—	—	—	—	0.02	0.02	—	—	n.d.	—	—
CaO	—	—	0.14	0.15	0.35	0.64	0.65	—	0.11	0.83	2.08	0.1
MnO	—	—	—	—	—	—	—	—	0.01	—	—	—
K <sub>2</sub> O	0.94	0.80	2.08	2.12	1.33	1.66	1.69	0.32	0.28	0.92	0.27	0.2
Na <sub>2</sub> O	2.25	2.20	1.38	1.42	2.93	0.63	0.64	1.88	2.14	2.65	—	2.3
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	—	—	—	—	—	0.88	tr.	—	n.d.
FeO	—	—	0.32	—	—	0.62	—	—	—	—	—	—
MgO	—	—	—	—	—	0.50	—	—	0.57	—	—	0.6
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Number of cations on the basis of 32 oxygen equivalents, ignoring H <sub>2</sub> O												
Si	11.72	11.78	11.13	11.27	10.90	11.44	11.47	11.03	11.05	11.31	11.29	11.25
Al	4.39	4.31	4.76	4.62	5.03	4.44	4.53	4.96	4.39	4.66	4.66	4.69
Ba	1.43	1.45	1.88	1.93	1.80	1.73	1.76	2.06	1.98	1.54	1.93	1.79
Sr	—	—	—	—	—	0.002	0.003	—	—	—	—	—
Ca	—	—	0.03	—	0.08	0.14	0.14	—	0.02	0.18	0.46	0.01
Mn	—	—	—	—	—	—	—	—	—	—	—	—
K	0.24	0.20	0.54	0.56	0.35	0.43	0.44	0.08	0.07	0.23	0.07	0.06
Na	0.86	0.84	0.54	0.58	1.17	0.25	0.25	0.77	0.86	1.03	—	0.89
Fe <sup>3+</sup>	—	—	—	—	—	0.11	—	—	0.14	—	—	—
Mg	—	—	0.09	—	—	0.15	—	—	0.17	—	—	0.18

1 — Glen Riddle (Meier 1939); 1' — analysis 1 calculated to 100% after deducting an estimated 1% of hydrargillite and an amount of hydrous magnesium silicate (white chlorite) equivalent to 0.27% of MgO; 2 — Iskra (Kostov 1962; *vide* Černý et al. 1977); 3 — Hrubšice (Černý, Povondra 1965); 3' — analysis 3 recalculated to 100% after deducting 1.68% stevensite and 0.58% "limonite" taken as FeO(OH); 4 — Ransko (Pokorný 1966 — *vide* Černý et al. 1977); 5 — Korsnäs (Sahama, Lahtinen 1967); 6 — Maungarahu (Black 1969); 7 — Andreasberg (Rinaldi et al. 1974; *vide* Gottardi, Galli 1985); 8 — Korsnäs, (Surdam 1971; *vide* Černý et al. 1977).

<sup>1</sup> At 110°C.

H<sub>2</sub>O contents in brackets — H<sub>2</sub>O by difference to approx. 100 wt.% total.

\* SEM images and EDS spectra corresponding to these analyses — see Figs 13A, B.

\*\* Number of cations — data after Černý et al. (1977).

tr. — traces; n.d. — not determined.

Potassium and sodium are both conspicuous in the chemical composition of the harmotome studied, with sodium predominating as is generally typical of this mineral (Table 2; also: Thugutt 1947; Sadanaga et al. 1961; Hansen 1991). Calcium, an element often reported in harmotome (Table 2; also: Thugutt 1947; Sadanaga et al. 1961; Rinaldi et al. 1974) was not found using EDS, nor was magnesium, iron or strontium. Additionally, the mineral analysed is characterized by distinctly higher amounts of silica and lower amounts of barium than those cited in the literature. These differences may reflect the presence of microcrystalline quartz inclusions in the harmotome crystals as suggested by the XRD and infrared results. It should be remembered, however, that the XRD detection limit for quartz is 0.5 wt.% (Pawloski 1985). The amount of non-structural Si is thus negligible and does not significantly affect recalculations of the chemical analyses. The chemical formulae of two crystals with element contents calculated on the basis of 32 oxygen atoms, are:



#### CLOSING REMARKS

Previous work on the red beds in the USCB (Kowalski 1977, 1979, 1982, 1983; Králík 1982; 1984; Klika 1998; Lipiarski et al. 1998, 2004) has shown that these beds reflect long-lasting, post-Carboniferous and pre-Miocene, supergene weathering of Carboniferous detrital-clay rocks, and of coals in which local, periodic fires had also occurred. These alterations were followed by burial of the beds under Miocene sediments and by later diagenetic and/or epigenetic changes. As a result, a number of neogenic minerals were formed of which the following have been detected in the red beds of the “Marcel” mine: clay minerals (smectite, halloysite  $-10 \text{ \AA}$  and  $-7 \text{ \AA}$ , kaolinite-D?, mixed-layered illite/smectite),  $\text{SiO}_2$ -group members (tridymite, cristobalite, microcrystalline quartz), harmotome, hematite, goethite, siderite, mullite, calcite, alunite and natroalunite, and rare chalcopyrite and sphalerite.

In the red beds of the “Marcel” mine, harmotome is the sole zeolite. It originated during the final stage of the evolution of the red beds. In some druses only does the younger mineral — dioctahedral smectite — overgrow the harmotome.

No occurrence of harmotome in red beds analogous to those in the USCB is known from elsewhere in the world. This mineral has been described almost exclusively from hydrothermal assemblages, both metasomatites and various types of infillings in rock vugs (e.g., Meier 1939; Russell 1946; Waterson 1953; Byström 1956; Černý, Povondra 1965; Sahama, Lehtinen 1967; Black 1969; Passaglia, Bertoldi 1983; Wieser 1985; also see: Deer et al. 1963; Gottardi, Galli 1985). Harmotomes of sedimentary origin, formed during diagenesis or weathering, are rare (Morgenstein 1967; Sheppard, Gude 1983; Gottardi, Galli 1985; Hay, Sheppard 2001). The harmotome described from the “Marcel” mine should belong, according to the conclusions of Kowalski (1981) and suggestions of

Gottardi and Galli (1985), to the latter sedimentary group. However, the “Marcel” harmotome formed as a result of the metasomatic alteration of aluminosilicate precursors and, later, crystallization from solutions in rock vugs. This harmotome could have originated during supergene weathering of Carboniferous strata previously thermally altered by coal fires or, later, during diagenesis of the weathered products after their burial under Miocene sediments about 200 m thick.

The source of barium, the element necessary in the formation of harmotome, is seen in pore waters which throughout the USCB, particularly in its SW part (the Rybnik area), are Ba-rich (Pałys 1966; Pluta, Pałys 1999; Pluta 2001). Highly mineralized chlorine-rich waters in the Carboniferous of this region commonly contain from several hundred to over 1,000 (maximum 2,400) mg Ba/dm<sup>3</sup>. As these waters are sulphate-free or contain only very low amounts of the sulphate ion, the formation of harmotome instead of barite was likely. According to Pałys (1966) and Pluta and Pałys (1999), the Ba enrichment of pore waters (brines) in the Carboniferous of the USCB could have been due to interaction with surrounding clay rocks containing the barium ion. The barium content of typical clay rocks ranges from 250 to 800 ppm Ba (Wedepohl 1978). Barium could also have been derived from feldspars, common in the Carboniferous detrital rocks. Rózkowska and Ptak (1995) suggest overlaying Miocene chemical sediments (evaporites) to be the most probable source.

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Marek MUSZYŃSKI, Piotr WYSZOMIRSKI

## HARMOTOM Z NOWEGO WYSTĄPIENIA PSTRYCH UTWORÓW W GÓRNOŚLĄSKIM ZAGŁĘBIU WĘGLOWYM (POLSKA)

### Streszczenie

W przeobrażonej brekcji zawałowej z nowego wystąpienia tzw. pstrych utworów w Górnośląskim Zagłębiu Węglowym w kopalni „Marcel” (Fig. 1) rozpoznano obecność harmotomu. W badaniach stosowano mikroskopię optyczną (Fig. 3–12), dyfrakcję rentgenowską (Tab. 2), spektroskopię absorpcyjną w podczerwieni (Fig. 15), SEM/EDS (Fig. 13) oraz analizę termiczną (Fig. 2). Harmotom jest składnikiem niektórych zmetasomatyzowanych klastów i lepiszcza brekcji oraz mikrodruz i wypełnień pustek skalnych. Słupkowe, subhedralne kryształy tego minerału z druz, przeważnie bezbarwne i przezroczyste, osiągają wielkość 0,5 mm. W przewodzie są to penetracyjne bliźniaki o symetrii pseudotetragonalnej (typ morwenitowy) i pseudorombowej (typ Marburg) (Fig. 3–12, 13 A, B; 14). Skład chemiczny harmotomu cechuje obecność zarówno potasu jak i sodu, przy zdecydowanej przewodzie tego ostatniego, oraz brak wapnia (Tab. 2, Fig. 13A, B). Wzory krystalochemiczne dwu analizowanych metodą EDS kryształów tego minerału są następujące:





Harmotom powstał w końcowym etapie formowania się pstrych utworów; jedynie miejscami występuje młodszy składnik — dioktaedryczny smektyt (Fig. 13C). Mogło to nastąpić jeszcze na etapie supergenicznego wietrzenia skał karbonu (uprzednio zmienionych termicznie skutkiem pożarów węgla) lub podczas późniejszej diagenety produktów tych przeobrażeń, po ich pogrzebaniu pod utworami miocenu. Źródłem baru były zasobne w ten pierwiastek, bezsiarczanowe lub ubogie w siarczanowy wody (roztwory) porowe występujące w karbonie tego rejonu.