THAUMASITE — A RARE MINERAL CONTAINING Si(OH)\(^{2-}\) GROUPS FROM DUBIE (THE DĘBNIK ANTICLINE, S POLAND)

**Abstract.** Detailed mineralogical investigation of exo- and endocontact rocks formed due to the emplacement of late Palaeozoic rhyodacite laccolith in carbonate sedimentary rocks, drilled in the Dębnik anticline near Dubie, revealed the presence of thaumasite Ca\(_3\)Si(OH)\(_6\)·12H\(_2\)O·(CO\(_3\))\(_2\)(SO\(_4\)). The thaumasite veins cut the rocks of the proximal zone of the highest temperature metamorphism, which extends few tens of meters within exocontact rocks (marbles) and one meter within rhyodacite. Apparently, the thaumasite formed as result of retrogression reactions from minerals contrived at the peak of metamorphism. High temperature calcium silicates reacted, at low temperatures, with basic waters containing carbonate and sulphate ions, allowing the changes of silicon coordination from Si\(^{IV}\) to Si\(^{VI}\). The thaumasite, calcite, aragonite and sepiolite veins belong to the last mineral generations formed in the Dębnik anticline. Thaumasite forms mineral paragenesis with calcite. To the best of our knowledge this is the first finding of this unique mineral in Poland.

**Key-words:** thaumasite, IR spectrum, contact metamorphism, retrogression, Dębnik anticline

**INTRODUCTION**

At the Dębnik anticline (Fig. 1) the late Palaeozoic rhyodacite intrusion (Muszyński et al., 1994) formed a 300 m thick contact aureole in the Devonian carbonate rocks (Narkiewicz, 1983). Contact metamorphism of dolomites led mainly to the formation of calcite-brucite marbles (Haranczyk, Wala 1989; Lewandowska 1989, 1998). The dolomites primarily contained a few intercalations enriched in siliceous, probably terrigenic material. In these siliceous zones neomineralization of lizardite, chrysotile (Lewandowska 1991), hydrotalcite (Muszyński, Wyszmierski 1998), grossular (Lewandowska, Rospondek 2000), and sepiolite (Lewandowska 1996) was observed. Rhyodacite itself is affected by the contact alterations only within a thin outermost zone where primary quartz-plagioclase-feldspar matrix was replaced by minerals of analcite group (Lewandowska et al. 2000). These exo- and endocontact rocks were cut by white, 

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thin veins, filled with fine crystalline mineral. From these veins, samples were selected (Fig. 2) for detailed mineralogical investigations, resulting in the first description of thuma-
site in Poland.

SAMPLES AND METHODS

Samples were collected from the Z-4 borehole core. The borehole was drilled be-

tween Dębik and Dubie villages near Kraków (Fig. 1). At the depths of 333.7 m and

369.0 m the rocks were cut by veins, from which mineral samples were handpicked for

further investigations (Fig. 2). The samples come from the veins cutting the exo-

(333.7 m) and endocontact rocks (369.0 m), respectively.

The samples were analysed by powder X-ray diffractometry (XRD) using a ho-

rizontal goniometer (HZG-4B), Cu-Kα radiation and Ni-filter. The observation of crys-

tals’ habit and elemental composition was performed with a JEOL 5410 scanning

electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS)

EDAX V-9800. Infrared absorption spectra (FTIR) were obtained at ambient tempera-

tures with 2.0 cm⁻¹ resolution in a range of 400–4000 cm⁻¹, using a BIO-RAD Fourier

Transform Spectrometer (FTS 135) equipped with a Michelson interferometer. The

air-dried, powdered samples were vacuum-pressed into KBr discs.

RESULTS

White, small crystals found are visible in rare veins (1–2 mm thick) at the depth

333.7 m and 369.0 m. In the sample from 333.7 m, i.e. 36 m away from the contact, the

vein, parallel to the axe of the core, is hosted by calcite-

-brucite marble (predazzite) over the length of 20 cm. In

this sample 1 cm wide nest was found (Phot. 1). In

the sample from 369.0 m, collected about 10 cm down

from the contact, another vein is hosted by the altered

rhyodacite.

The veins are filled with white crystals with vitreous luster. The crystals are up to 0.1 mm long and up

0.03 mm wide. Their habit is well visible in scanning electron microscope images (Phot. 2 and 3). The

hexagonal prismatic crystals are doubly terminated with partly developed hexagonal pyramids in the sample

from the exocontact void (Fig. 3). The pyramids are better developed for the large specimens, while smaller

are entirely prismatic.

In thin section the mineral is colourless. Cleavage was not observed. Crystals are often automorphic, uniaxial (at Phot. 4 some crystals were cut perpendicularly

through vein. The crystals are up to 0.3 mm long and a few

through vein. The crystals are up to 0.3 mm long and a few

Fig. 3. Habitus of the thuma-
site crystals separated from voids
(sample from 333.7 m)
to z-axis and therefore appear isotropic) and negative. They exhibit negative relief against the mounting medium (n = 1.54). The described geometrical and optical features are consistent with those of thumasite. Thumasite refractive indices are n_e = 1.468 and n_o = 1.506 ± 0.002, and the birefringence Δ = 0.04 (e.g. Carpenter 1963). The birefringence herein observed was in this range.

This identification was positively confirmed by the XRD analysis. X-ray diffraction pattern (Fig. 4) is analogous to that of the specimen from Ballyvalton, Northern Ireland (card 23-0128 JCPDS), with the main reflections at 9.55 Å (100), 5.51 Å (40) and 3.41 Å (20). Additionally, a small admixture of calcite was detected.

![Fig. 4. XRD pattern of the thumasite, numbers denote d_hkl [Å] (sample from 333.7 m)](image)

A further evidence for thumasite identification in Dubie comes from the comparison of its infrared absorption spectrum (Table 1 and Fig. 5) with the reference spectrum of thumasite from Paterson, New Jersey, USA (Moenke 1966). The wavenumber values for most of the absorption bands are in good agreement (Table 1), however, in the range of the O-H bond stretching frequencies (3600–3400 cm⁻¹), there are few differences. The band at 3560 cm⁻¹, described by Moenke (1966), was not observed in the Dubie thumasite here (Table 1 and Fig. 5). This difference can be related to the presence of ettringite in the reference material due to the existence of solid solution between these minerals (Kollmann, Strübel 1981). For mixed thumasite-

<table>
<thead>
<tr>
<th>Localization</th>
<th>Dubie (Z-4 depth 333.7 m)</th>
<th>Dubie (Z-4 depth 369.0 m)</th>
<th>Paterson, New Jersey, USA*</th>
<th>Paterson, New Jersey, USA***</th>
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<tr>
<td>Assignment**</td>
<td>Absorption bands</td>
<td>[cm⁻¹]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>v (O-H)</td>
<td>not observed</td>
<td>not observed</td>
<td>3560</td>
<td>not observed</td>
</tr>
<tr>
<td>v (O-H)</td>
<td>3502</td>
<td>3503</td>
<td>3500</td>
<td>3503</td>
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<tr>
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<tr>
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<td>3430</td>
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<tr>
<td>v (O-H)</td>
<td>3405</td>
<td>3404</td>
<td>3403</td>
<td>3403</td>
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<tr>
<td>v (O-H)</td>
<td>3240</td>
<td>3235</td>
<td>3240**</td>
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<tr>
<td>δ H-O-H</td>
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<td>1696</td>
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<td>1696</td>
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<tr>
<td>v (a) CO₃</td>
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<td>1398</td>
<td>1400</td>
<td>1396</td>
</tr>
<tr>
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<td>1101</td>
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<tr>
<td>v (a) SO₄</td>
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<tr>
<td>SiO₄</td>
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<tr>
<td>δ CO₃</td>
<td>883</td>
<td>877</td>
<td>887</td>
<td>886</td>
</tr>
<tr>
<td>v Si-O in Si(OH)₆</td>
<td>749</td>
<td>747</td>
<td>750</td>
<td>746</td>
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<td>771</td>
<td>765</td>
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<tr>
<td>δ SO₄</td>
<td>638</td>
<td>639</td>
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<tr>
<td>δ SO₄</td>
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<td>501</td>
<td>500</td>
<td>500</td>
<td>499</td>
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</table>

** Varma, Bensted (1973) and Bensted, Varma (1974).
*** Thumasite from the collection of Mineralogical Museum, Institute of Geological Sciences, Jagiellonian University.
ettringite crystals such an absorption band at ca. 3600 cm\(^{-1}\) was observed indeed, whereas pure thauasite had no such a band (Kollmann, Strübel 1981). This band becomes prominent in the spectrum of ettringite. Such a band is also noted in hydrated calcium silicates. Unfortunately the data on the composition of the reference thauasite (Moenke 1966) are not available. In addition to these bands there are bands at ca. 2860, 3050, 3240 cm\(^{-1}\) repeatedly observable for the Dubie thauasite. These bands were also recorded for a specimen from Paterson, New Jersey, from the institute muséal collection. This range is usually omitted in the data published, however some of these bands (specially at ca. 3250 cm\(^{-1}\)) are easily recognizable at the published spectra (e.g. Bensted, Varma 1974; Kollmann, Strübel 1981).

The spectrum of thauasite in the data base (Win IR Search provided with the BIO-RAD IR spectrometers) is inconsistent neither with those published by Moenke (1966) and Kollmann and Strübel (1981) nor with the data obtained herein.

The elemental analysis (EDS) showed the presence of Si, S and Ca (Fig. 6) confirming that the mineral does not form solid solution with ettringite.

\section*{DISCUSSION}

Thauasite is a hydrated calcium silanol-carbonate-sulphate mineral. Its name is derived from the Greek “thauasmos” — surprising (Knill, Young 1960). Surprisingly, it is one of a few known substances where Si coordinates six hydroxyl groups. Due to its features Strunz (1978) classified thauasite into a separate class of nesosilicates. Thauasite crystal structure was determined by Edge and Taylor (1969, 1971) revealing that it contains silanol groups Si(OH)\(^{2+}\). However, even before the thauasite X-ray structure determinations had been accomplished (Edge, Taylor 1969; 1971), Moenke (1964) concluded from the comparison of the stishovite SiO\(_2\) and thauasite infrared spectra that the Si was six-coordinated. This coordination records in the IR spectra as absorption bands at 501, 673 cm\(^{-1}\) resulting from Si\(^{IV}\)-O bending and a broad band at 749–771 cm\(^{-1}\) from Si\(^{IV}\)-O stretching (Bensted, Varma 1974) for the Dubie thauasite. Furthermore, presence of an extremely tiny amount of four-coordinated silica (Si\(^{IV}\)-O) is recorded as a weak band at 937 cm\(^{-1}\) (Table 1) (Varma, Bensted 1974). This is apparent that the Dubie thauasite is very pure phase.

Thauasite consists of Ca[(H\(_2\)O)\(_4\)(OH)\(_4\)]\(^{12+}\) and Si(OH)\(^{2+}\) polyhedra, sharing common edges, running parallel to the z-axis, which are connected to sulphate and carbonate groups by hydrogen bonding (Effenberger et al. 1983; Jacobsen et al. 1996). Probably due to this bonding sulphate and, specially, carbonate stretching vibration are shifted towards relatively low frequency ranges. The water particles of Ca[(H\(_2\)O)\(_4\)(OH)\(_4\)]\(^{12+}\) polyhedra are unequal, one of the four has planar threefold coordination of oxygen surrounded by Ca and two H atoms, whereas three other have oxygen tetrahedrally coordinated with Ca, two H of water and another from hydrogen bond (Effenberger et al. 1983). Due to the existence of strong hydrogen bonding of the water molecules, the (H-O) stretching vibrations are shifted towards relatively low frequency ranges. These are recorded as bands at ca. 2860, 3050, 3240 cm\(^{-1}\). The differences in structural position of water must have resulted in the split of the water bending vibrations observed in a range of 1650–1700 cm\(^{-1}\).

Due to the structural features of thauasite, the chemical formula is often written: Ca\(_3\)[Si(OH)\(_6\)] \(\cdot\) 12H\(_2\)O\(_4\)(CO\(_3\))\(_2\)(SO\(_4\)) (Effenberger et al. 1983). The mineral is hexagonal belonging to the space group P6\(_3\)/m (hexagonal dipyramids).

Thauasite is a rare mineral noted from sulphide deposits and skarns. In Sweden it is known from thermally metamorphosed carbonates hosting sulphides in Längban, Skottvångs and Viscaria (Knill, Young 1960). In similar rocks, it was found in England (High Sedling Mine, Weardale, County Durham, and in Shap, Cumbria) (Young et al. 1998) as well as in the Baikal region of Russia [in veinlets of the wollastonite-garnet
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THAUMASYT — RZADKI MINERAŁ ZAWIERAJĄCY GRUPY Si(OH)₆⁻ Z DUBIA (ANTYKLINA DĘBNIKA, S POLSKA)

Streszczenie

Szczegółowe badania mineralogiczne skał egzo- i endokontaktowych, powstałych w wyniku oddziaływania późnopaleozoicznej intruzji ryodacytowej na dewońskie skały węglanowe, doprowadziły do identyfikacji thaumasytu Ca₃[Si(OH)₆]·12H₂O[(CO₃)₃(SO₄)] występującego w trąbcach te skały żylach. Źyły thaumasytu przecinają utwory strefy najwyższej temperatury przeobrażeń, która to strefa obejmuje kilkadziesiąt metrów aureoli egzokontaktowej oraz około jednego metra skał endokontaktowych. Thaumasyt powstawał w procesach retrogresywnych przeobrażeń, kosztem minerałów uformowanych w temperatury piku metamorfizmu. Wysokotemperaturowe krzemiany wapnia reagowały w niskich temperaturach z zasadowymi wodami zasobnymi w jony wapnia oraz jony siarczanowe, umożliwiając zwarcie koordynacji krzemionki z Si⁴⁺ na Si⁶⁺. Thaumasyt w paragenезie z kalcytem, oraz aragonit i sepiolit tworzą ostatnie generacje minerałów żyłowych w skałach przeobrażonych antykkliny Dębnika. Niniejsza praca dokumentuje pierwsze stanowisko występowania tego unikalnego minerału w próbkach geologicznych w Polsce.
Katarzyna GODYN1, Marek MUSZYŃSKI1

AN UNUSUAL FRACTION OF HEAVY MINERALS FROM THE LOWER CARBONIFEROUS OF WESTERN POMERANIA (NW POLAND)

Abstract. The fraction of heavy minerals, separated out of the Lower Carboniferous, volcanogenic lithic wacke (Brdą-2 borehole, 2208.5 m, NW Poland) was studied using optical microscopy, SEM/EDS, XRD and IR. This fraction, making up as much as 4.7 wt.% of the 0.49–0.03 mm grain fraction, is composed of pseudoturite, anatase, brookite, rutile, pyrite, phosphate bioclasts and microconcretions (?), zircon, apatite, traces of biotite and tourmaline. Opaque minerals, particularly oxides of Fe and Ti (with dominating pseudoturite) representing pseudomorphoses after ilmenite, strongly prevail. Most of the heavy minerals originated on a not so distant land by weathering of volcanites of the rhyolite-dacite-trachydacite type and — probably — also of those poorer in silica. Pseudoturite, the characteristic component of the fraction studied, originated as a result of supergene alterations of ilmenite in a hot and humid climate, either directly in volcanites or after deposition of ilmenite in a beach environment. As pseudoturite is metastable, it could have been preserved due to relatively fast burial in the sediment and reducing and neutral or slightly alkaline conditions during its diagenesis. Pseudoturite, which is a common mineral in contemporary beach sand deposits of "ilmenite" in tropics, has not been described so far in the rocks of Poland.

Key-words: pseudoturite, heavy minerals, volcanogenic lithic wacke, Lower Carboniferous, Western Pomerania, NW Poland

INTRODUCTION

In the course of investigations of the heavy minerals from the Lower Carboniferous strata of Western Pomerania (Muszyński et al. 2001), the authors noticed a fraction of heavy minerals significantly different in its qualitative and quantitative composition from other fractions. The fraction was separated out of a volcanogenic lithic wacke, belonging — according to Matyja et al. (2000) — to the Tournaisian Kurowo Oolite Limestone Formation. The wacke, only several cm thick, was tapped in the Brdą-2 borehole at a depth of about 2208.5 m, within a fifteen or so metres thick complex of clay shales and sandstones with inlets of dolomites. This complex is under- and overlain by oolithic limestones, usually with an admixture of clastic material of the aleuritic size, dolomitized to a different degree (Fig. 1).

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A. LEWANDOWSKA, M. ROSPONDEK — Thaumasite — a rare mineral containing Si(OH)62− groups from Dubie (the Dębnik Anticline, S Poland)