

Mariusz ROSPONDEK<sup>1</sup>, Anna LEWANDOWSKA<sup>1</sup>

**COMPARATIVE FT-IR SPECTRAL STUDIES OF THAUMASITE**  
**Ca<sub>3</sub>Si(OH)<sub>6</sub>(CO<sub>3</sub>)(SO<sub>4</sub>)·12H<sub>2</sub>O**

INTRODUCTION

Thaumasite is a relatively rare hydrated calcium silanol-carbonate-sulphate mineral Ca<sub>3</sub>Si(OH)<sub>6</sub>(CO<sub>3</sub>)(SO<sub>4</sub>)·12H<sub>2</sub>O. Its name is derived from the Greek "*thaumasion*" meaning surprising. It is the only known substance, where six hydroxyl groups coordinate silicon Si(OH)<sub>6</sub><sup>-2</sup>. X-ray structural investigation revealed that thaumasite consists of Ca[(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>4</sub>]<sup>2-</sup> and Si(OH)<sub>6</sub><sup>-2</sup> polyhedra, sharing common edges, running parallel to the z-axis, which are connected to sulphate and carbonate groups by hydrogen bonding (Edge, Taylor 1971; Effenberger et al. 1983; Jacobsen et al. 2002). Even before the determination of the thaumasite structure had been accomplished (Edge, Taylor 1971), Moenke (1964) concluded from the comparison of the stishovite <sup>VI</sup>SiO<sub>2</sub> and thaumasite infrared spectra that the thaumasite silicon was six-coordinated. The infrared (IR) absorption spectra of thaumasite were usually published in a limited wavelength range (Moenke 1966, Bensted, Prakash Varma 1974; Kollmann, Strübel 1981; Krivolutskaya 1984), which did not cover the conventionally accessible IR analytical range. Since that time the FT-IR technique has been developed allowing one to obtain spectra with higher resolution. Herein, thaumasites from four different localities were subjected to FT-IR spectral analyses in the range 400-4000 cm<sup>-1</sup>, resulting in the record of reproducible spectra revealing a series of yet not described absorption bands.

SAMPLES AND METHODS

The investigated samples of thaumasite originate from four localities:

1. Dubie, the Dębnik anticline near Kraków, Poland (for details see: Lewandowska, Rospondek 2002).
2. Paterson, New Jersey, U.S.A. from the museal collection of Institute of Geological Sciences, Jagiellonian University, and belonging to the collection of K. Chrobak from 1932 year. This was provided by Dr. E. Koszowska.
3. Viscaria, Kiruna, Lappland, Sweden.
4. Lierskogen, Norway. The last two samples originate from skarn deposits, and were donated by Dr. Göran Axelsson from his private collection.

Infrared absorption spectra (FTIR) were obtained with a 2.0 cm<sup>-1</sup> resolution in

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<sup>1</sup>Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland; e-mail: ros@geos.ing.uj.edu.pl

the range of 400-4000  $\text{cm}^{-1}$ , 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

The microscopical identification and the minerals purity were confirmed by the XRD powder analysis. X-ray diffraction patterns are analogues to that of the specimen from Ballyalton, Northern Ireland (card 23-0128 JCPDS).

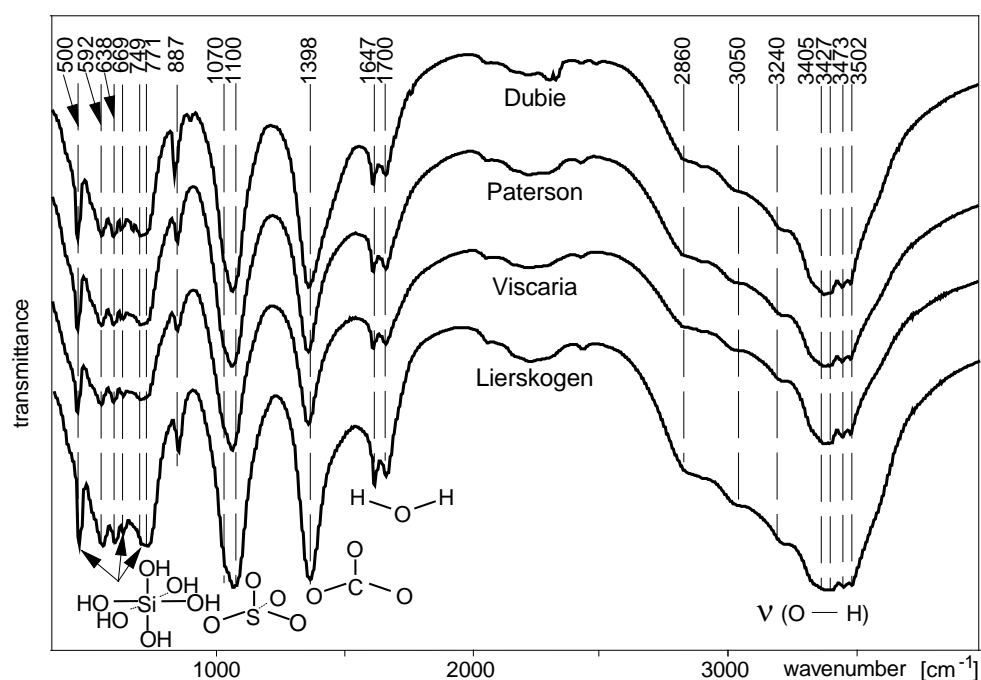


Fig. 1. The comparison of IR absorption spectra of the thauasites investigated.

Most of the IR absorption bands are well reproducible among investigated thauasite specimens (Fig. 1 and Table 1). In the IR spectra the six-fold coordination of the thauasite silicon is recorded as absorption bands at 500 and 669  $\text{cm}^{-1}$  resulting from  $\delta(\text{VI Si-O})$  bending and a broad band at 749-771  $\text{cm}^{-1}$  from  $\nu(\text{VI Si-O})$  stretching (Bensted, Prakash Varma 1974). The thauasite sulphate groups are recorded as bands at 592 and 638  $\text{cm}^{-1}$  resulting from  $\delta \text{SO}_4^{2-}$  and 1070 and 1100  $\text{cm}^{-1}$  resulting from  $\nu(\text{a}) \text{S-O}$  of  $\text{SO}_4^{2-}$ . The carbonate groups are recorded as bands at 887  $\text{cm}^{-1}$  resulting from  $\delta \text{CO}_3^{2-}$  and 1398  $\text{cm}^{-1}$  resulting from  $\nu(\text{a}) \text{C-O}$  of  $\text{CO}_3^{2-}$  as shown by Bensted, Prakash Varma (1974).

Nevertheless, there are few differences noted in the range of the O-H bound stretching frequencies. The band at 3560  $\text{cm}^{-1}$  e.g. assigned to thauasite by Moenke (1966) was not observed in none of the thauasites investigated. Such a band is present in some hydrated calcium silicates. Appearance of the band at ca.

Table 1. Position of the IR absorption bands for thaumasite.

Assignment of absorption bands	Paterson, New Jersey, USA*	Paterson, this investigation	Dubie***	Dubie, this investigation	Visc-aria	Liers-kogen
	[cm <sup>-1</sup> ]					
v (O-H)	3560*	not observed	not observed	not observed	not observed	not observed
v (O-H)	3500*	3504	3502	3503	3504	3503
v (O-H)	3470*		3473		3471	3470
v (O-H)	3420*	3425,	3427	xxx	3426	3402
	not menti.*	xxxx	3405,	3404,	xxx	3402
v (O-H)	not menti.* 3240**	3251	3237	3239	3239	3233
v (O-H)	not menti.*	3062	3052	3056	3061	3056
v (O-H)	not menti.*	2878		2890	2878	2869
δ H-O-H	1705*	1696	1700	1696	1700	1696
δ H-O-H	1660*	1648	1647,1605	1647	1647	1648
v (a) CO <sub>3</sub>	1400*	1396	1398	1397	1396	1396
v (a) SO <sub>4</sub>	1102*	1100	1100	1101	1099	
v (a) SO <sub>4</sub>	1075*	weak	1070 (weak)		weak	1102
v Si-O SiO <sub>4</sub>	non, 935*		907, 937	937	not observed	strong
δ CO <sub>3</sub>	887**	886	883	877	886	886
v Si-O in Si(OH) <sub>6</sub> <sup>2-</sup>	750, 765*	746	749, 771	747 712	745	767
v Si <sup>IV</sup> -O in Si(OH) <sub>6</sub> <sup>2-</sup>	673*	669	673	669	669	669
δ SO <sub>4</sub>	640**	639	638	639	639	639
δ SO <sub>4</sub>	590**	589	592	591	589	589
δ Si-O in Si(OH) <sub>6</sub> <sup>2-</sup>	500*	499	501	500	499	500
δ Si-O in Si(OH) <sub>6</sub> <sup>2-</sup>		weak	470	weak	weak	weak

\* Moenke (1966); \*\* Bensted Prakash Varma (1974); \*\*\* Lewandowska & Rospondek (2002)

3600 cm<sup>-1</sup> may be related to the presence of ettringite in mixed thaumasite-ettringite crystals (Kollmann, Strübel 1981). Furthermore, this investigation

resulted in the record of additional absorption bands at ca. 2860, 3050, 3240  $\text{cm}^{-1}$ . These are repeatedly recorded for all of the thaumasite specimens (Fig. 1). These bands can result from the  $\nu(\text{O-H})$  vibrations in water, which are shifted towards much lower energies due to the formation of strong hydrogen bonds. This contrasts with the Edge's & Taylor's opinion (1971) that there are no strong hydrogen bonds in thaumasite. However, detail structural investigation by Jacobsen et al. (2002) revealed that such bonds are relatively short, and varying in length from 1.67 to 2.23Å. Furthermore, the higher resolution of the FT-IR technique revealed a split of the band at 3400  $\text{cm}^{-1}$  (Moenke, 1966) into two bands at 3405 and 3427  $\text{cm}^{-1}$  as well as the 3470  $\text{cm}^{-1}$  (Moenke, 1966) into 3052 and 3473  $\text{cm}^{-1}$ . The spectrum of thaumasite 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, Strübel (1981) nor with the data obtained herein.

#### CONCLUSIONS

The wave number values for most of the recorded absorption bands and among the variety of investigated thaumasite specimens are in good agreement (Fig. 1). However, this investigation resulted in the record of additional absorption bands at ca. 2860, 3050, 3240  $\text{cm}^{-1}$  originating from the  $\nu(\text{O-H})$  vibrations of molecular water. The shift towards lower energy must result from the formation of strong hydrogen bonds of molecular water with oxygen of  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$ . The band at 3560  $\text{cm}^{-1}$  previously assigned to thaumasite (Moenke 1966) is not observable for pure thaumasites.

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