

*On the infra-red spectrum and thermal decomposition products of thaumasite,<sup>1</sup>  $\text{Ca}_3\text{H}_2(\text{CO}_3/\text{SO}_4)\text{SiO}_4 \cdot 13\text{H}_2\text{O}$*

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*Summary.* The infra-red spectrum of untreated thaumasite



as well as the spectra and X-ray diffraction patterns of thaumasite heated in air at 200, 360, 550, 725, 800, 900, and 1150° C were investigated. The release of CO<sub>2</sub> and H<sub>2</sub>O upon heating was followed. It was established that thaumasite changes between 200 and 550° C to a glass-like, amorphous state. Ca<sub>2</sub>SiO<sub>4</sub>-polymorphs and anhydrite are formed upon heating at temperatures up to 800° C. From 900° C calcium silicosulphate and anhydrite are the thermal decomposition products. These results are used in the assignment of the IR-absorption bands under 1400 cm<sup>-1</sup> of untreated thaumasite, which are shown to be of a composite nature, i.e. attributable to overlapping vibrations of both sulphate and silicate tetrahedra.

COMPLEX silicate-sulphate-carbonate compounds are an appealing field of application for infra-red (IR-) spectra. Since IR-spectroscopy became a major mineralogical tool several papers have been devoted to such compounds, mainly in the hope of casting light on controversial problems related with the co-ordination of a given atomic species. However, it should be obvious that a purely IR-approach to such problems contains many pitfalls. This statement is illustrated by the interpretation recently given for the IR-spectrum of thaumasite, Ca<sub>3</sub>H<sub>2</sub>(CO<sub>3</sub>/SO<sub>4</sub>)SiO<sub>4</sub>·13H<sub>2</sub>O. Thaumasite is a relatively rare mineral, but it has a highly interesting composition and a structure that merits closer scrutiny. It should be mentioned that the structure of this mineral was

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determined in 1956 by X-rays by Welin, who found silicon and sulphur in the usual fourfold coordination and carbon in plane threefold coordination. On the other hand, Moenke (1964) published in a short note the IR-spectrum of thaumasite and came to the conclusion that silicon enters the thaumasite structure in an octahedral sixfold coordination; his argument was supported by wave number coincidences with the IR-spectrum of stishovite,  $\text{SiO}_2$ , whose structure was determined by Stishov and Belov (1962) in terms of an octahedral coordination of silicon and whose IR-spectrum was studied by Lyon (1962) and Sclar (1962). Thus the vibrational assignments given by Moenke for the IR-absorption bands of thaumasite are strongly at variance with the structure as proposed by Welin.

The present investigation was undertaken in order to test the reliability of IR-data in assessing the coordination of silicon and sulphur in the structure of thaumasite. To this effect the thermal decomposition products of thaumasite up to  $1150^\circ\text{C}$  were subjected to X-ray and IR-studies. On heating and subsequent transformations of the mineral the absorption bands of its IR-spectrum undergo drastic changes in wave number and intensity and eventually resolve into bands or band complexes characteristic of the different phases formed during the heating process. The assumption was that if the vibrational frequencies of two kinds of discrete functional groups coincide and give rise to only one absorption maximum, the latter would resolve upon heating into several groups of non-overlapping bands, thus allowing the identification of the groups involved in the initial relevant absorption bands of the untreated material.

During the course of our investigations we were also confronted by other as yet unsolved problems connected with the breakdown of the thaumasite structure on heating and with the pathways followed by the decomposition process.

*Experimental methods and results.* Thaumasite from Igljka, Elhovo district, south-east Bulgaria, was used in the present work. The mineral was found in monticellite skarns with merwinite, garnet, idocrase, calcite, and wollastonite. It forms veins up to 5 to 6 cm thick and occurs as parallel fibrous aggregates (Kostov *et al.*, 1964).

Different samples were heated for an hour in air at 200, 360, 550, 725, 800, 900, and  $1150^\circ\text{C}$ . The starting material and the thermal decomposition products were investigated by X-ray powder photographs taken with a cylindrical 57.3 mm Debye-Scherrer camera. A diffractometer pattern was also taken of the material heated at  $1150^\circ\text{C}$ . IR-spectra

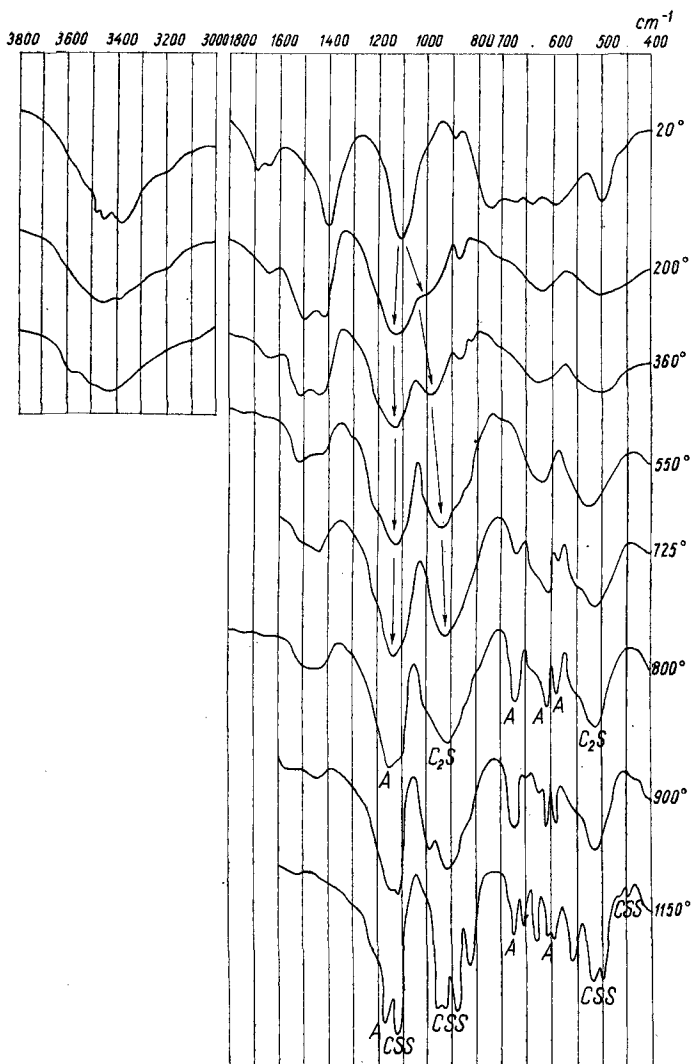


FIG. 1. Infra-red spectra of thaumasite and of its thermal decomposition products. A, absorption bands of  $\text{CaSO}_4$ ;  $\text{C}_2\text{S}$ , of  $\text{Ca}_2\text{SiO}_4$ ; CSS, of calcium silicosulphate.

were recorded on a UR-10 Zeiss Jena spectrometer between 400 and  $1800\text{ cm}^{-1}$  and 3000 to  $3800\text{ cm}^{-1}$ . The spectra are given in fig. 1.

The kinetics of the release of  $\text{CO}_2$  during the heating experiments were investigated by heating the sample in an air current, which was passed

through a column filled by an absorbing agent that is coloured under the influence of the carbon dioxide. The amount of  $\text{CO}_2$  released was estimated by the progression of the boundary of the coloured portion of the column. The curve obtained in this way is given in fig. 2.

The wave numbers of the absorption bands of the thaumasite from Bulgaria coincide with those given by Moenke for thaumasite from

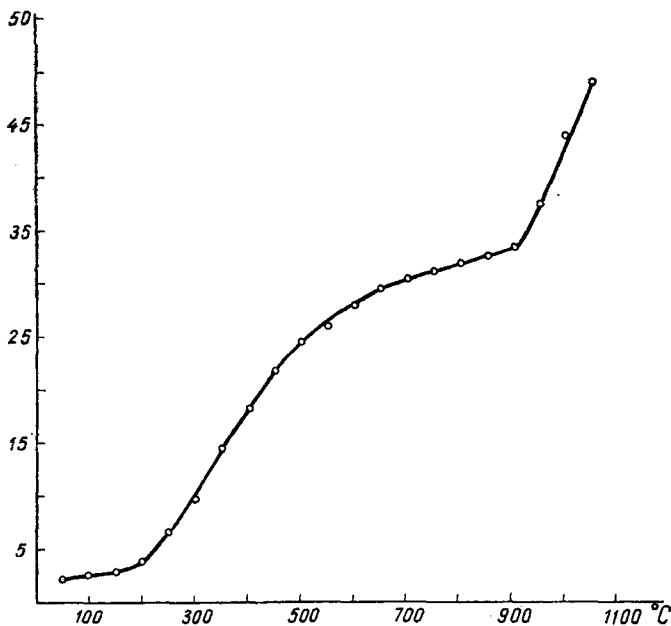


FIG. 2. Curve of release of  $\text{CO}_2$  upon heating at atmospheric pressure. Ordinates are given in arbitrary units.

Paterson, New Jersey. According to well-known data and in agreement with Moenke, some of the bands can be immediately and unambiguously assigned to vibrations of particular functional groups. This applies to all bands lying at frequencies higher than  $1100\text{ cm}^{-1}$  ( $\text{CO}_3$  and  $\text{H}_2\text{O}$ ). However, the situation with the bands lying in the frequency range  $1100\text{--}400\text{ cm}^{-1}$  is, as will be shown later, considerably more intricate.

Let us consider successively the character of the products obtained on heating at different temperatures.

At  $200$  and  $360^\circ\text{ C}$  the bands of  $\nu_{\text{OH}}$  in the region  $3000$  to  $3700\text{ cm}^{-1}$  merge into one broad absorption band, which has disappeared at  $550^\circ\text{ C}$ . The two bands of the  $\delta_{\text{OH}}$  at about  $1660$  and  $1705\text{ cm}^{-1}$  give at  $200^\circ\text{ C}$

one band at approximately  $1650\text{ cm}^{-1}$ , which has also disappeared at  $550^\circ\text{C}$ .

From  $200$  to  $725^\circ\text{C}$  a general broadening of the remaining IR-absorption bands occurs, which seems to indicate a transformation to a glass-like state. This is supported by the over-all features of the X-ray diffraction patterns, in which several broad and diffuse rings are observed, accompanied by faint but relatively sharp lines. Between  $360$  and  $725^\circ\text{C}$  the decomposition products are completely X-ray amorphous.

Thus the first step in the transformation of thaumasite is the change to a glassy, X-ray amorphous state at  $200^\circ\text{C}$ , which persists up to  $550^\circ\text{C}$ . This process is accompanied by the elimination of the water molecules, as indicated by the decrease in intensity and eventual vanishing of the OH-stretch bands located between  $3400$  and  $3500\text{ cm}^{-1}$  in untreated thaumasite. This process is already completed at about  $500^\circ\text{C}$ .

The behaviour of the  $\nu_3(a)$  band of  $\text{CO}_3$  at  $1400\text{ cm}^{-1}$  is particularly interesting. At  $200^\circ\text{C}$  there is a splitting of this band into two components with approximately equal intensity at  $1495$  and  $1430\text{ cm}^{-1}$ . From  $200$  to  $550^\circ\text{C}$  these bands persist with variable intensity ratio. From  $550$  to  $725^\circ\text{C}$  the band at  $1495\text{ cm}^{-1}$  gradually vanishes. From  $725^\circ\text{C}$  onwards both  $\text{CO}_3$ -absorption bands appear with a very low intensity, but continue to be present up to about  $1020^\circ\text{C}$ .

Contrary to previous opinions (Zhabin, 1957, and Font-Altaba, 1960) the present work shows that carbon dioxide is continuously released during thermal treatment over a large temperature interval. This was established by the above modified gas-chromatographic technique and by the behaviour of the band of the  $\text{CO}_3$  groups ( $1400\text{ cm}^{-1}$ ). The curve given in fig. 2 shows that the most active elimination of carbon dioxide takes place between  $200$  and  $500^\circ\text{C}$  and between  $900$  and  $1150^\circ\text{C}$ . On the other hand, the peculiar behaviour of the  $1400\text{ cm}^{-1}$  band is more difficult to understand. While the over-all decrease in intensity is obviously connected with the release of  $\text{CO}_2$ , the splitting of the absorption band and the reversal in the intensity ratio of the two components remains to be accounted for; comparison between the frequencies of these bands and those reported for the different calcium carbonates yields interesting results: Indeed, the first band coincides with the stretch band of  $\text{CO}_3$  in calcite, while the second one coincides with the same vibration in vaterite (Weir and Lippincott, 1961); it can therefore be safely assumed that both calcite and vaterite appear during thermal

decomposition of thaumasite. The intensity ratio reversal must obviously be connected with the different amounts of each carbonate phase formed at different temperatures.

The strong and sharp band of untreated thaumasite at  $1100\text{ cm}^{-1}$  with its very weak shoulder at  $1075\text{ cm}^{-1}$  splits already at  $200^\circ\text{ C}$  into two absorption maxima centred at  $1140\text{ cm}^{-1}$  and  $1015\text{ cm}^{-1}$ . Up to  $550^\circ\text{ C}$  the separation between these two maxima increases up to a point when they are located at  $1160$  and  $960\text{ cm}^{-1}$  with approximately equal intensity. At  $725^\circ$ , and particularly at  $800^\circ\text{ C}$ , there is a clear splitting of the  $1160\text{ cm}^{-1}$  band in two components at  $1155$  and  $1120\text{ cm}^{-1}$ , which become sharper as the heating temperature increases and which coincide with the two stretch bands of anhydrite.

At the same time the second broad band at  $950\text{ cm}^{-1}$  also splits. At  $800^\circ\text{ C}$  two shoulders appear at about  $1000$  and  $850\text{ cm}^{-1}$  which give rise at higher temperatures to sharp bands at  $952$ ,  $930$ , and  $880\text{ cm}^{-1}$  with a shoulder at  $900\text{ cm}^{-1}$ .

The identification of the bands lying at frequencies lower than  $1100\text{ cm}^{-1}$  in the spectra of the thermal decomposition products is, however, rather difficult. Whereas at  $800^\circ\text{ C}$  the IR-spectra and the X-ray patterns clearly show the presence of the different polymorphs of  $\text{Ca}_2\text{SiO}_4$  and of  $\text{CaSO}_4$ , at  $900^\circ$ , and particularly at  $1100^\circ\text{ C}$  the picture changes radically and its interpretation would require the coexistence in the mixture of almost all modifications of calcium silicate, which is hardly probable, taking into account the widely differing stability fields of the different polymorphic modifications of this compound.

In this respect the investigation of the material heated at  $1150^\circ\text{ C}$  provided highly significant results, which eventually led to a satisfactory solution of the problem. Indeed, the X-ray diffractometer pattern (table I) indicated clearly that the material consisted in fact of anhydrite and a calcium silicosulphate closely related to that described by Gutt and Smith (1966) and formulated  $(2\text{CaO}\cdot\text{SiO}_2)_2\cdot\text{CaSO}_4$ . This is very likely, since after thermal elimination of the volatile components the bulk composition of the remaining product of thaumasite is  $\text{Ca}_{6.24}\text{Si}_{1.94}\text{S}_{2.03}\text{O}_{16}$ , which can be assumed to decompose further according to the scheme  $\text{Ca}_{6.24}\text{Si}_{1.94}\text{S}_{2.03}\text{O}_{16} \rightarrow \text{CaSO}_4 + \text{Ca}_{5.24}\text{Si}_{1.94}\text{S}_{1.03}\text{O}_{12}$ , or approximately  $\text{CaSO}_4 + (2\text{CaO}\cdot\text{SiO}_2)_2\cdot\text{CaSO}_4$ . It is of interest to point out that our heating experiment at  $1150^\circ\text{ C}$  resulted in the formation of a light-green product, which seems to resemble closely the compound found by Sundius and Petersen (1960; cited by Gutt and Smith, 1966) in cement rotary kilns and which yields an X-ray pattern similar to that of

TABLE I. X-ray diffraction pattern of thaumasite heated at 1150° C, as compared with the data for calcium silicosulphate and anhydrite

1		2		3		1		2		3	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
—	—	8.51	5	—	—	2.292	60	2.287	5	—	—
7.70	50	7.71	5	—	—	2.221	20	2.230	4	—	—
5.80	50	—	—	—	—	2.206	60	2.201	4	2.208	20
5.70	60	—	—	—	—	2.179	70	2.169	5	2.183	8
5.35	20	5.34	4	—	—	2.134	5	2.136	3	—	—
4.59	80	4.57	8	—	—	2.123	5	2.119	3	—	—
4.26	40	4.24	3	—	—	2.087	50	2.083	3	2.086	9
4.20	40	—	—	—	—	2.067	20	2.061	5	—	—
4.09	60	4.08	7	—	—	2.022	50	2.022	3	—	—
4.06	40	—	—	—	—	2.009	5	2.015	4	—	—
3.97	50	—	—	—	—	1.996	20	—	—	1.993	6
3.95	60	3.95	7	—	—	1.962	70	1.958	6	—	—
3.87	40	—	—	3.87	6	1.954	50	1.947	3	—	—
3.86	30	3.85	3	—	—	1.939	5	—	—	1.938	4
3.613	30	3.60	3	—	—	1.924	5	1.926	3	—	—
3.504	100	—	—	3.498	100	1.897	90	1.895	9	—	—
3.346	90	3.34	7	—	—	1.894	90	1.891	9	—	—
3.197	90	3.19	9	—	—	1.872	40	—	—	1.869	15
3.135	70	3.12	7	3.118	3	1.858	5	—	—	1.852	4
3.045	60	3.04	7	—	—	1.850	20	1.848	3	—	—
3.003	50	2.99	7	—	—	1.838	40	1.837	5	—	—
2.990	70	2.98	7	—	—	1.823	20	1.820	4	—	—
2.853	100	2.844	10	2.849	33	1.804	40	1.804	5	—	—
2.830	100	2.825	10	—	—	1.781	60	1.780	4	—	—
2.799	20	2.797	3	2.797	4	1.776	30	1.775	4	—	—
2.740	30	2.740	3	—	—	1.756	70	1.754	6	—	—
2.703	20	2.703	3	—	—	1.751	40	—	—	1.749	11
2.620	80	2.611	8	—	—	1.748	50	1.748	4	1.748	10
2.566	90	2.564	9	—	—	1.742	40	1.739	4	—	—
2.474	40	2.479	4	2.473	8	1.713	40	1.710	3	—	—
—	—	2.382	3	—	—	1.698	60	1.698	6	—	—
2.343	30	2.354	3	—	—	1.674	10	1.676	3	—	—
2.322	10	—	—	2.322	22	1.650	40	—	—	1.648	14

1. Thaumasite from Igljka, Bulgaria, heated at 1150° C.
2. Calcium silicosulphate, after Gutt and Smith (1966).
3. Anhydrite.

(2CaO.SiO<sub>2</sub>)<sub>2</sub>.CaSO<sub>4</sub>. Obviously the absorption bands observed in the IR-spectrum of thaumasite heated at 1150° C belong to anhydrite and to the calcium silicosulphate.

*Conclusions.* The experiments described in the preceding section give a reasonably faithful and complete picture of the transformations to which thaumasite is subjected upon heating in air up to 1150° C.

The detailed identification of the thermal decomposition products of thaumasite shows that none of the absorption bands appearing in untreated material at a frequency lower than  $1400\text{ cm}^{-1}$  can be unambiguously assigned to vibrations of either sulphate or silicate discrete groups. This clearly follows from the behaviour of these bands on heating, which indicates that all the above-mentioned bands are of a composite nature, i.e. they must be assigned simultaneously to the vibrations of sulphate tetrahedra and silicate groups. This immediately invalidates Moenke's assignment, while it does not contradict Welin's finding of discrete silicate tetrahedra in the structure of thaumasite. Indeed, the separation of absorption bands due to two different kinds of  $XO_4$  groups on the sole basis of the IR-spectrum appears to be a quite insoluble problem. This was to be expected since the two groups give rise to absorption bands that lie in the same spectral range. The solution of this problem has been attempted by Schwarcz and Speelman (1965) for scapolite by recording the IR-spectrum of the mineral at liquid nitrogen temperature in the hope of resolving the main absorption bands into more bands indicating the presence of both sulphate and silicate groups. However, their attempt was unsuccessful.

It has been argued that the presence in the IR-spectrum of untreated thaumasite of bands that could not be assigned to  $XO_4$  tetrahedra supports the presence of  $SiO_6$ -octahedra. This argument appears fallacious. While it is possible that any additional bands could arise from vibrational interaction between both kinds of  $XO_4$  groups, it is highly improbable that they are due to the presence of  $SiO_6$ -octahedra on the sole basis of wave number coincidences and neglecting other important factors, such as the composition and the conditions of formation of thaumasite, which would seem to preclude the presence of silicon in such an unusual coordination as the octahedral one.

The above example should make it clear that in the case of complex compounds containing more than one kind of discrete functional group having the same configuration, the investigation of the thermal decomposition products yields a considerable and highly useful, though indirect, amount of information.

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