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THE THERMAL DECOMPOSITION OF THAUMASITE FROM MOTHAE KIMBERLITE PIPE, LESOTHO, SOUTHERN AFRICA

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The endothermic decomposition of thaumasite from Mothae which has been investigated by DTA and TG shows a peak temperature of 138–203°, and reaction orders of 0.45–1.00, depending on the heating rate employed. The activation energy of the reaction was found to be about 19 kcal/mole; the enthalpy is 246 cal/g.

The decomposition seems to be divided into one reaction with $n = 0.90$, immediately followed by one with $n = 1.59$. The first reaction is attributed to the loss of H_2O, the second one to the (partial) release of OH and CO_2.

Thaumasite, $[Ca_3Si(OH)_6 \cdot 12\,H_2O](SO_4)\,(CO_3)$, is one of the rare cases, where silica occurs in octahedral co-ordination [1–3]. Thaumasite is found in low-temperature and low-pressure parageneses [4–7].

The thermal decomposition of thaumasite has previously been investigated by Badalov and Golovanov [8], Zhabin [9], Font-Altaba [10], and Kirov and Poulieff [11]. The aim of the present contribution is a more detailed investigation of the decomposition reaction, with special emphasis on reaction kinetics.

Material and methods

The thaumasite used for this study is found as soft, white fibrous masses, forming veinlets within the "blue ground" kimberlite of Mothae pipe (Northern Lesotho). It most likely represents a very late-stage mineral, and occurs with zeolite minerals, apophyllite, vermiculite and saponite.

For the differential thermal analyses, Linseis (L-72) and Netzsch DTA equipment have been used, the latter for the curves given in Fig. 1. Analytical details are given in Figs 1–3 and Table 1 respectively. For thermogravimetry a Stanton thermobalance has been used.

Results and discussion

The general DTA curve of thaumasite is, according to Font-Altaba [10], characterized by a large endothermic peak at 206° (loss of water and carbon dioxide), and a small exothermic effect at 709° (crystallization of larnite + anhydrite). Similar results have been obtained by Badalov and Golovanov [8], Zhabin [9], and Ivanovna [12], who adds small endothermic effects at about 1030° and 1230° (reversible reaction) to the pattern. Federico [13] records endothermic reactions at 170°, 770°, 1260° and 1360°, and minor exothermic effects at 835° and 985°.

Our results (Fig. 1), measured in CO_2 flow, show the major endothermic effect at 168°, a minor peak at 675° and a larger effect at 1306°. The only exothermic peak appeared at 817°. On cooling, a small endothermic peak was found at 800°. The DTA pattern in air was similar to the above-mentioned curve. There is, however, an endothermic reaction at 1085°, in agreement with the curve given by Ivanovna [12].

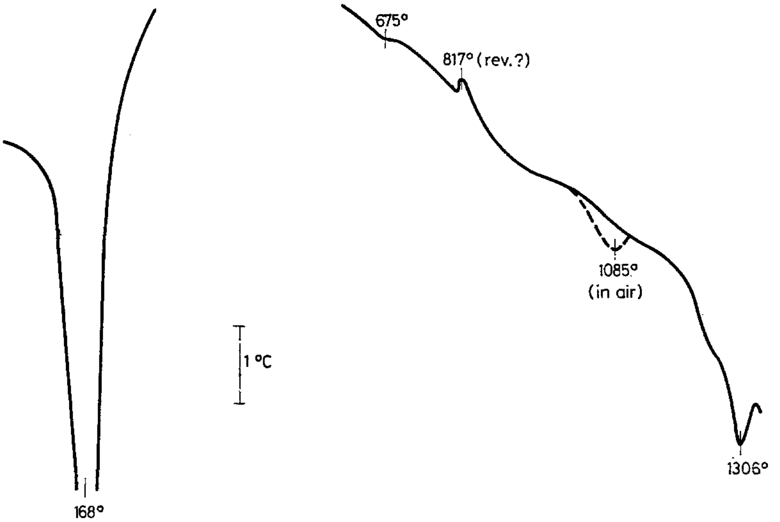

Fig. 1. DTA curve of thaumasite. Heating rate: 10°/min; 15 l/h CO_2, Al_2O_3 crucibles; 50 mg sample, 138 mg alumina as reference material

The main endothermic effect has been studied more closely. The peak temperature was found to increase with increasing heating rate: 1°/min – 138°, 5°/min – 153°, 10°/min – 166°, 20°/min – 173°, 50°/min – 203°. The value of 206.6 given by Font-Altaba [10] suggests that a heating rate of about 50°/min has been employed. This author also describes the decomposition of thaumasite to be a first-order reaction. Our investigations show that this is only true for heating rates of 20°/min; slower heating rates render lower reaction orders (Table 1).

The main endothermic effect is composite in its nature. In most of our runs, the peak might be approximated with a single reaction taking place. If heating rates of about 20°/min or more are employed, the composite nature of the reaction becomes evident (Fig. 2). If the reaction orders are evaluated according to Fig. 2, a value of 0.90 is obtained for the first, and 1.59 for the second reaction (Table 1).

Table 1

Kinetic parameters of the decomposition of thaumasite (Mothae)

Heating rate, °/min	Reaction order, n
1	0.45
5	0.64
10	0.80
20	1.00
20	0.90 first reaction
20	1.59 second reaction

Activation energy (various methods), E_a *kcal/mole*

Method	No of points	Correlation	E_a^x	k	Crucible
Kissinger [14]	3	1.00	19.3	$2.6 \cdot 10^9$	alumina
Kissinger	5	0.99	20.7	$8.1 \cdot 10^9$	platinum
Piloyan et al. [15]	6	1.00	12.0		alumina
Piloyan 1st reaction	6	0.99	17.2		platinum
Piloyan 2nd reaction	5	0.98	12.9		platinum
Coats et al. [16]	5	1.00	13.2[1]		alumina

[1] assuming $n = 1$ (see above)

Enthalpy: $\Delta H = 246$ cal/g (reference: In, latent heat of melting, 6.8 cal/g)

The enthalpy of the (combined) reaction was determined to be 246 cal/g. The latent heat of fusion for indium (6.8 cal/g) was used for calibration. The activation energy of the reaction was determined to be in the order of 12–21 kcal/mole; a value of 19±2 kcal/mole seems most satisfactory (Table 1). The difference in activation energies for the first and second reaction, as defined in Fig. 2, falls within the limits of error for the method employed (Table 1).

Thermogravimetric analysis up to 800° in static air (Fig. 3a) shows a total weight loss of 47.4%, in good agreement with previously published data [8, 10, 13]. The weight loss on heating up to 230° – beyond the main decomposition – amounts to 37.8%. From this temperature up to 550°, a continued minor loss is recorded (Fig. 3a), followed by a still smaller loss up to 750°. This is in contrast to the statement by Font-Altaba [10,] that no weight loss occurs in the temperature range from 330 to 1000°. Still, our results are confirmed both by the study of Federico [13], and the data on carbon dioxide evolution given by Kirov and Poulieff [11]. They found that CO_2 evolution commences at about 200°, and continues up to 1150°, with maxima at 200–500°, and 900–1150°. Also, DTA curves obtained by us are in favour of continued minor reactions occurring throughout the whole temperature range investigated. We never obtained a zero-line as reproduced by Font-Altaba [10] (Fig. 1).

Thermogravimetric analysis carried out with CO_2 flowing over the sample (Fig. 3b) shows a total weight loss of 39% up to 550°, as compared with 45% loss on heating the material to the same temperature in air (Fig. 3a). This difference might be attributed by CO_2 being retained in the amorphous material formed by the decomposition of thaumasite [11] due to the CO_2 atmosphere. Also, a small "saddle" is seen within the main decomposition reaction (Fig. 3b), as is expected by the inhibitive action of the CO_2 atmosphere upon the release of CO_2 from the sample.

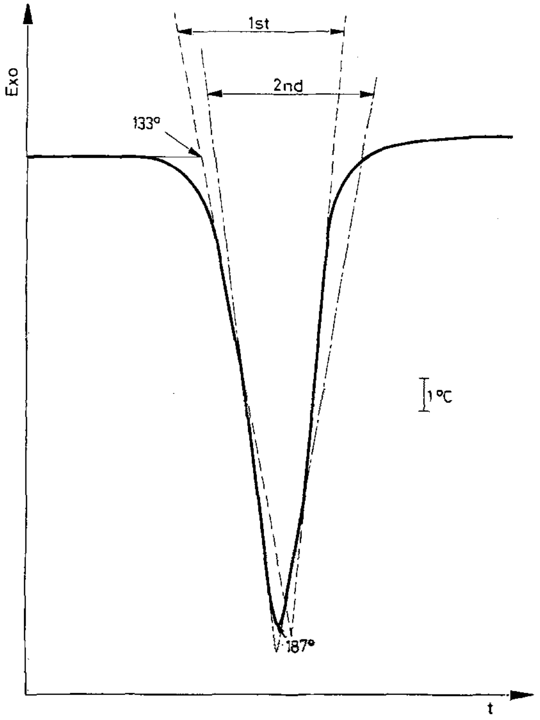

Fig. 2. The decomposition of thaumasite. Heating rate 20°/min; static air, Pt crucibles, 10.2 mg sample, 8.0 mg alumina as reference material

The structure of thaumasite, as determined by Edge and Taylor [3], is characterized by $[Ca_3Si(OH)_6 \cdot 12\ H_2O]^{4+}$-columns parallel to *c*. In between, CO_3^{2-} and SO_4^{2-} groups are located. It seems highly unlikely that both H_2O, OH, and CO_2 are to be released at the same event. It is therefore suggested – supported by the results of Kirov and Poulieff – that the first reaction (Fig. 2) is to be identified with H_2O release from the structure, the second, immediately succeeding reaction, with the release of OH and CO_2. The latter reaction is not completed during the main event, but, as indicated by DTA and TG curves and the above quoted results obtained by Kirov and Poulieff, continues to far higher temperatures. The release

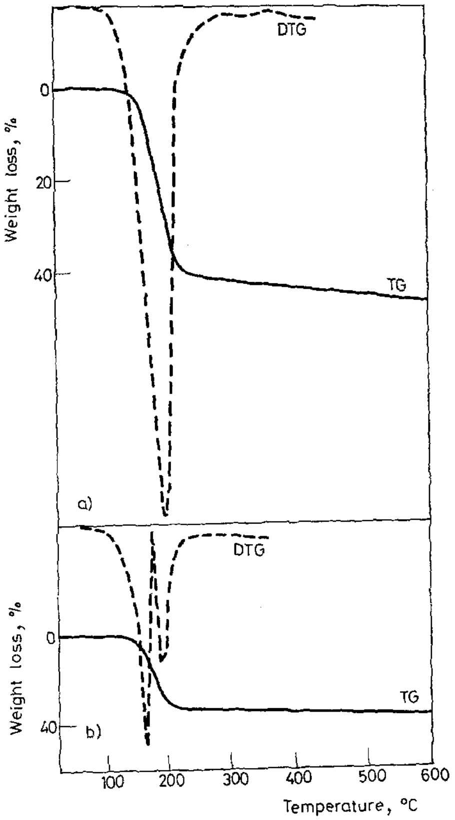

Fig. 3. TG curves of thaumasite. Heating rate 6°/min. *a*) 141 mg sample, static air; *b*) 58 mg sample, 15 l/h CO_2.

of OH groups is completed prior to the crystallization of larnite + anhydrite (about 700°), while CO_3^{2-} groups are still retained at that temperature [11].

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RÉSUMÉ — La décomposition endothermique de la thaumasite de Mothae a été étudiée par ATD et TG. Suivant la vitesse de chauffage utilisée la température au sommet du pic varie de 138 à 203° C et l'ordre de réaction de 0.45 à 1.00. On a trouvé que l'énergie d'activation s'élevait à 19 kcal. mol^{-1} et l'enthalpie à 246 cal. g^{-1}.

Il semble que la décomposition s'effectue suivant une réaction d'ordre $n = 0.90$, immédiatement suivie par une autre où $n = 1.59$. On attribue la première réaction à la perte d'eau et la seconde à la libération (partielle) d'hydroxyles OH et d'anhydride carbonique CO_2.

ZUSAMMENFASSUNG — Die durch DTA und TG überprüfte endothermische Zersetzung von Thaumasit aus Mothae zeigt in Abhängigkeit der angewandten Aufheizgeschwindigkeiten Spitzentemperaturen zwischen 138 und 203° C, sowie Reaktionsordnungen von 0.45 bis 1.00. Die Aktivierungsenergie der Reaktion ergab sich zu 19 Kcal/Mol, die Enthalpie zu 246 cal/g.

Die Zersetzung scheint in eine Reaktion von $n = 0.90$ und eine sofort darauffolgende von $n = 1.59$ geteilt zu sein. Die erste Reaktion wird dem Verlust von H_2O, die zweite der (teilweisen) Freisetzung von OH und CO_2 zugeschrieben.

Резюме — Эндотермическое разложение таумасита из Моте, которое было исследовано помощью ДТА и ТГ, показало пик при температуре 138—203° и порядок реакции 0,45—1,00 в зависимости от скорости нагрева. Было найдено, что энергия активации должна быть около 19 ккал/моль, энтальпия — 246 кал/г. Кажется, что разложение разделяется на одну реакцию с $n = 0{,}90$, за которой немедленно следует реакция с $n = 1{,}59$. Первая реакция приписана потере воды, а вторая — частичному выделению OH и CO_2.