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THERMAL ANALYSIS, X-RAY DIFFRACTION AND INFRARED SPECTROSCOPIC STUDY OF SYNTHETIC BROCHANTITE

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Pure brochantite was prepared at 60° from 0.5 *M* copper(II) sulphate and sodium hydroxide solutions at pH 8.0. The decomposition products arising when it was heated at different temperatures were identified using X-ray diffraction analysis and infrared spectroscopy. Dolerophanite, $CuO.CuSO_4$, which is invariably reported to be formed during the thermal decomposition of brochantite (of both synthetic and mineral origins), was not formed at any stage of the decomposition in the present case. The sequence of decomposition is

$$CuSO_4.3Cu(OH)_2.xH_2O \xrightarrow{80\text{–}170^\circ} CuSO_4.3Cu(OH)_2 + xH_2O$$

$$CuSO_4.3Cu(OH)_2 \xrightarrow{250\text{–}400^\circ} CuSO_4.2Cu(OH)_2 + CuO + H_2O$$

$$CuSO_4.2Cu(OH)_2 \xrightarrow{610\text{–}700^\circ} 3CuO + 2H_2O + SO_2 + {}^1/_2O_2$$

The higher pH conditions adopted here for the precipitation are probably responsible for the above mechanism of decomposition.

Even though much work has been done on the thermal characteristics of copper sulphate [1–6], very little information is available on the thermal behaviour of basic sulphates of copper, especially brochantite [7–11]. In the case of brochantite prepared from $CuSO_4$ and NaOH, Margulis [7] observed three endothermic peaks, at 295, 390 and 842°, while Miranov [9] noticed three endothermic (120, 355 and 510°) and two exothermic peaks (250–310° and 560–575°). For the compound prepared by using KOH (instead of NaOH), Pannetier et al. [8] reported one exothermic (500°) and three endothermic peaks (120, 300 and 800°).

As the above results show a large variance and as the compositions of the basic sulphates formed depend markedly on the experimental conditions used for the preparation, it was felt that some systematic work had to be undertaken on this compound for a complete understanding of its thermal behaviour. This paper

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reports the preparation and thermal behaviour of pure brochantite and the characterisation of its thermal decomposition products by means of X-ray diffraction and I.R. spectroscopy.

Experimental

Brochantite was precipitated by the addition of a 0.5 *M* copper sulphate (BDH AnalaR) solution at 60° to a solution of sodium hydroxide (SM GR) kept at pH 8.0 and at the same temperature. The mixture was stirred continuously and its pH was kept constant througnout the precipitation. The precipitate was aged overnight and washed with distilled water until the washings had a pH of <7.0 and were completely free from sulphate. The gel sample was then dried in air at 30°. It is designated SO in this paper.

Thermal analysis was carried out by using a suitable amount of the sample (200 mg) in a derivatograph (MOM, Hungary) over the temperature range 30–1000° at a heating rate of 10 deg/min. A DRON–I (USSR) X-ray diffractometer was used to obtain X-ray diffractograms of the samples. The filtered X-radiations Cu K_α and Mo K_α were used and the X-ray generator was operated at 30 kV and 10 mA. Infrared spectra were taken on a Perkin–Elmer 237B spectrophotometer in the range 4000–625 cm^{-1}, using nujol as mulling agent.

Results and discussion

The X-ray diffraction data on the air-dried sample (SO) are given in Table 1. A comparison of the data on SO with the standard XRD lines of brochantite, langite, antlerite, dolerophanite, tenorite and copper hydroxide [2, 12] shows that SO exhibits intense X-ray diffraction lines characteristic of brochantite only. 100% intense XRD lines of langite (6.9 Å), dolerophanite (3.63 Å), antlerite (4.86 Å), tenorite (2.32 Å) and copper(II) hydroxide (3.73 Å), as well as the other important lines of these, which do not interfere with those of brochantite are absent from the sample. Hence, sample SO is pure brochantite. The infrared spectrum of sample SO closely resembles that of brochantite [13, 14] and shows all the peaks corresponding to it; it differs markedly as regards the shapes and peak positions of langite [13, 14] antlerite [13–15], dolerophanite [11, 14], copper hydroxide [16] and copper oxide [17]. Thus, these results confirm that sample SO is pure brochantite.

DTA of sample SO (Fig. 1) shows three endotherms, around 110° (range 80–180°), 360° (range 240–420°) and 690° (range 610–700°), and two exotherms, at 200° (range 170–240°) and 450° (range 430–470°). In order to identify the different products formed at various temperatures and to study the sequence of decom-

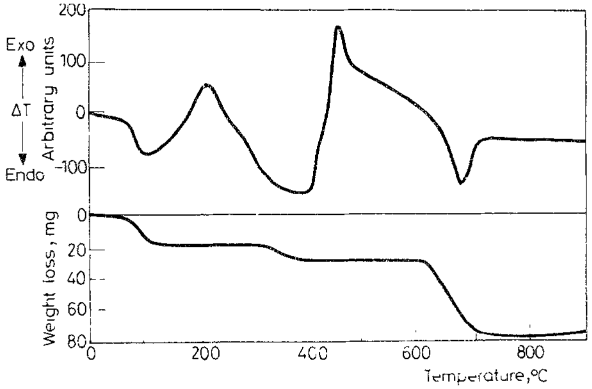

Fig. 1 DTA and TG of brochantite sample heated in air. Weight of sample used = 200 mg

Table 1 Relative intensities of X-ray diffraction lines of synthetic brochantite heated to different temperatures

Sl. No.	d, Å	Samples							
		S0	S2	S3	S4	S5	S6	S7	S8
1.	6.80	—	—	1.0	4.0	4.5	4.5	—	—
2.	6.38	42.2	46.5	5.5	—	—	—	—	—
3.	6.01	—	—	—	3.6	4.0	6.0	—	—
4.	5.40	27.8	33.1	4.5	4.5	5.0	5.0	—	—
5.	4.86	—	—	7.5	15.6	18.0	19.1	—	—
6.	3.90	59.6	60.6	14.8	—	—	—	—	—
7.	3.60	—	—	—	10.6	12.5	14.0	—	—
8.	3.19	30.8	30.3	4.5	—	—	—	—	—
9.	2.93	13.6	14.7	—	—	—	—	—	—
10.	2.75	—	—	—	—	—	—	3.9	10.5
11.	2.683	—	—	5.2	7.1	8.2	24.0	—	—
12.	2.678	47.8	60.6	17.0	—	—	—	—	—
13.	2.523	100	100	100	100	100	100	100	100
14.	2.323	8.3	11.3	37.0	93.1	94.9	95.2	100	100
15.	2.266	12.9	21.7	—	—	—	—	—	—
16.	2.19	20.4	26.1	11.1	—	—	—	—	—
17.	1.87	—	—	—	26.8	27.9	28.0	29.2	30.0
18.	1.74	37.2	40.8	30.0	—	—	—	—	—
19.	1.72	—	—	—	11.2	11.3	11.4	11.6	12.5
20.	1.67	10.2	10.7	—	—	—	—	—	—

position, sample SO was heated at different temperatures (100, 200, 250, 300, 400, 500, 600, 700, 800 and 1000°) for 2 hours. The samples thus obtained are designated S1, S2, S2*, S3, S4, S5, S6, S7, S8 and S10, respectively, and their X-ray data and infrared spectra are given in Table 1 and Fig. 2, respectively.

Sample S2 shows XRD lines corresponding to brochantite, while S3 exhibits the lines of brochantite, antlerite and copper oxide (Table 1). Sample SO is pale-green in colour and changes to brownish-black when heated beyond 300°. Samples heated at 100, 200 and 250° exhibit infrared spectra similar to that of brochantite (Fig. 2). Hence, it is evident that the first endotherm, at 100°, is due to the loss of adsorbed water molecules, while the first exotherm, at 200°, is probably due to the rystallization of brochantite.

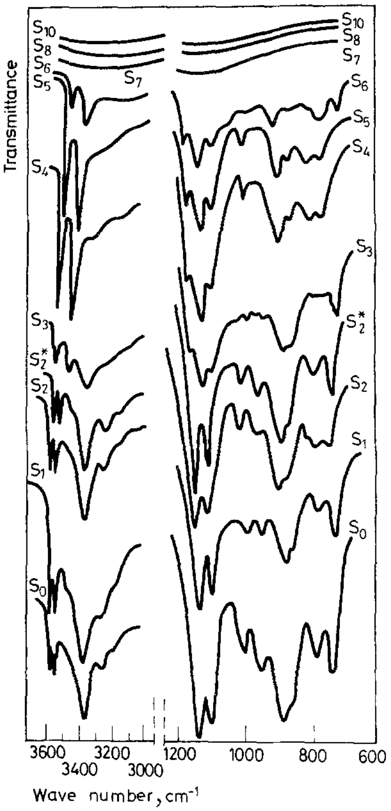

Fig. 2 Infrared spectra of brochantite sample heated to different temperatures (S0 — 30°; S1 — 100°; S2 — 200°; S2* — 250°; S3 — 300°; S4 — 400°; S5 — 500°; S6 — 600°; S7 — 700°; S8 — 800°; S10 — 1000°)

Sample S3 exhibits X-ray diffraction lines corresponding to brochantite, antlerite and copper oxide (Table 1) and not those of dolerophanite. The distortion of the peaks of brochantite by the presence of antlerite is also clearly evident in the infrared spectrum of this sample. Samples heated at 400, 500 and 600° show X-ray diffraction lines of only antlerite and copper oxide. The infrared spectra of these samples show the presence of antlerite and the absence of brochantite and dolerophanite. Thus, the endotherm observed in the temperature range 200 to 430° in the DTA of sample

SO must be due to the conversion of brochantite to antlerite and copper oxide above 250°, while the exotherm between 400 and 600° may be due to the crystallization of antlerite. This is also evident in the X-ray diffractograms of these samples, where the peaks corresponding to antlerite increase in intensity as the sample is continuously heated to 600°. This view is also supported by thermogravimetry (Fig. 1), which shows no loss in weight between 430 and 600°.

The sample heated at 600° (S6) gives X-ray diffraction lines corresponding to antlerite and copper oxide, while the samples heated at 700, 800 and 1000° (S7, S8 and S10) show the presence of copper(II) oxide only. The infrared spectra of samples S7, S8 and S10 do not show the presence of antlerite or dolerophanite. Hence, it can be concluded that the endotherm at 690° is due to the decomposition of antlerite to copper(II) oxide.

Calculations based on the weight losses in the TG curves indicate that the formula of the brochantite sample (SO) is $CuSO_4.3Cu(OH)_2.3.5\,H_2O$. The sequence of decomposition, as indicated by thermal, X-ray and infrared spectral analyses of the products at different stages, is

$$CuSO_4.3Cu(OH)_2.3.5H_2O \xrightarrow{80\text{–}170^\circ} CuSO_4.3Cu(OH)_2 +$$

$$+3.5\,H_2O$$

$$CuSO_4.3Cu(OH)_2 \xrightarrow{250\text{–}400^\circ} CuSO_4.2Cu(OH)_2 + CuO +$$

$$+H_2O$$

$$CuSO_4.2Cu(OH)_2 \xrightarrow{610\text{–}700^\circ} 3\,CuO + 2\,H_2O + SO_2 +$$

$$+{}^1/_2\,O_2$$

It is interesting at this stage to mention the sequence of decomposition of brochantite reported by earlier workers. From their results in the thermal study of copper hydroxide sulphates of various compositions, Margulis and coworkers [10] concluded that dolerophanite is formed, but not antlerite, and they reported the formula of brochantite as $(CuO.CuSO_4).(n-1)\,Cu(OH)_2.H_2O$, where n varies from 2 to 3. In the thermoanalytical studies by Ramamurthy and Secco [11] and Pannetier et al. [8], brochantite was found to decompose to dolerophanite between 250 and 400°, but no formation of antlerite was reported. Vandael and Vanthournhout [18] studied the copper patina obtained in urban atmospheres which mainly consists of brochantite by thermal analysis and reported that antlerite is formed at 280–380°, which is converted to dolerophanite between 415 and 550°. Brochantite minerals from the Soviet Union [19] also showed the formation of dolerophanite around 530°, which finally gave copper oxide around 900°.

In this study, however, the presence of dolerophanite could not be detected at any stage of the decomposition of brochantite, either by X-ray diffraction or by infrared spectroscopy. This is also substantiated during DTA beyond 700° by the absence of any endothermic peak corresponding to the decomposition of dolerophanite. Further, it is significant to note that mixtures of brochantite and copper oxide prepared by increasing the pH up to 10.5 did not form dolerophanite at any stage of the thermal decomposition either (unpublished work of the authors). The present behaviour in the mechanism of decomposition is probably due to the precipitation of brochantite at a comparatively high pH (viz. 8.0), which resulted in the formation of $CuSO_4.3Cu(OH)_2.xH_2O$ and not $(CuO.CuSO_4).(n-1)Cu(OH)_2.H_2O$ as suggested by Margulis et al.

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Zusammenfassung — Reines Bronchantit wurde bei 60° und pH 8 aus Lösungen von Kupfer(II)-sulfat (0.5 M) und Natriumhydroxid hergestellt. Die beim Erhitzen auf verschiedene Temperaturen entstehenden Zersetzungsprodukte wurden röntgendiffraktometrisch und infrarotspektroskopisch identifiziert. Dolerophanit, $CuO.CuSO_4$, das bei der thermischen Zersetzung von sowohl synthetischem als auch natürlich vorkommendem Bronchantit gebildet werden soll, konnte nicht als Produkt einer der Zersetzungsstufen nachgewiesen werden. Die Reihenfolge der Zersetzung ist:

$$CuSO_4.3Cu(OH)_2.xH_2O \xrightarrow{80-170^\circ} CuSO_4.3Cu(OH)_2 + xH_2O$$

$$CuSO_4.3Cu(OH)_2 \xrightarrow{250-400^\circ} CuSO_4.2Cu(OH)_2 + CuO + H_2O$$

$$CuSO_4.2Cu(OH)_2 \xrightarrow{610-700^\circ} 3\,CuO + 2\,H_2O + SO_2 + {}^1/_2\,O_2$$

Резюме — Чистый брокантит был получен при 60° из 0,5 молярных растворов сульфата двухвалентной меди и гидроокиси натрия при pH = 8. Продукты разложения, образующиеся при нагревании его при различных температурах, были идентифицированы рентгенофазовым анализом и ИК спектроскопией. Долерофанит, $CuO.CuSO_4$, являющийся устойчивым соединением и должен был бы образовываться при термическом разложении как синтетического, так и минерального брокантита, в настоящем случае не образовывался на всех стадиах разложения. Последовательность разложения брокантита может быть представлена следующими уравнениями реакций:

$$CuSO_4.3Cu(OH)_2.xH_2O \xrightarrow{80-170^\circ} CuSO_4.3Cu(OH)_2 + xH_2O$$

$$CuSO_4.3Cu(OH)_2 \xrightarrow{250-400^\circ} CuSO_4.2Cu(OH)_2 + CuO + H_2O$$

$$CuSO_4.2Cu(OH)_2 \xrightarrow{610-700^\circ} 3CuO + 2H_2O + SO_2 + 1/2\,O_2$$