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Thermal decomposition reactions of caledonite and their products

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ABSTRACT. The thermal decomposition of caledonite has been examined by simultaneous differential thermal analysis, thermogravimetry and mass spectrometry. Structural H_2O and CO_2 are liberated endothermically between 300 and 400 °C leaving a residue of lead sulphate, oxysulphate, and Cu(I) and Cu(II) oxides. A series of sharp endothermic peaks between 850 and 950 °C correspond to phase transition and melting reactions of the PbO-$PbSO_4$ mixture. The sulphate anion breaks down above 880 °C. Mass spectra of the gaseous decomposition products show SO_2, SO, and O_2, although SO is an artefact arising from ion fragmentation of the SO_2 within the mass spectrometer. The residue at 1060 °C is composed predominantly of $2PbO \cdot PbSO_4$ and Cu(I) and Cu(II) oxides.

KEYWORDS: caledonite, differential thermal analysis, thermogravimetry, mass spectrometry.

A NUMBER of papers have recently been devoted to the characterization of and distinction between the polymorphs of $Pb_4SO_4(CO_3)_2(OH)_2$ (Russell *et al.*, 1983, 1984; Livingstone and Sarp, 1984) and the thermal decomposition of the most common of these—leadhillite—has been comprehensively described by Milodowski and Morgan (1984). The present paper describes the reactions undergone by the related mineral caledonite ($Pb_5Cu_2(SO_4)_3(CO_3)(OH)_6$) on heating, using results from simultaneous DTA-TG equipment linked to a quadrupole mass spectrometer for evolved volatiles analysis.

Description and initial characterization of sample

The caledonite occurred in the centre of a geode approximately 4 cm in diameter, from the Leadhills district, Strathclyde Region, Scotland (British Geological Survey, mineral inventory no. 7443). It was present as prismatic bluish-green crystals, elongated along (001), intergrown with anglesite and minor linarite. The caledonite crystals were carefully hand-separated under a binocular microscope and ground to pass a 120 mesh (125 μm) screen. The ground material gave an X-ray powder pattern almost identical with that recorded on JCPDS card 29-565A (see also Giacovazzo *et al.*, 1973). The infra-red spectrum of the material was recorded by Dr J. D. Russell who reported (personal communication, March 1985) that it 'is identical to that over the range 1800-400 cm^{-1} shown by Moenke (1974). The principal OH stretching band occurs at 3408 cm^{-1} with weak inflexions at 3434, 3377, and 3300 cm^{-1}, compared to the positions listed by Moenke at 3625, 3585, and 3410 cm^{-1} but not illustrated. There was little or no interaction between the mineral and the alkali halide, the spectrum (fig. 1) being virtually identical to those obtained in inert mulling agents, the latter showing only slight weakening of SO_4 absorption bands at 1120 and 620 cm^{-1}.'

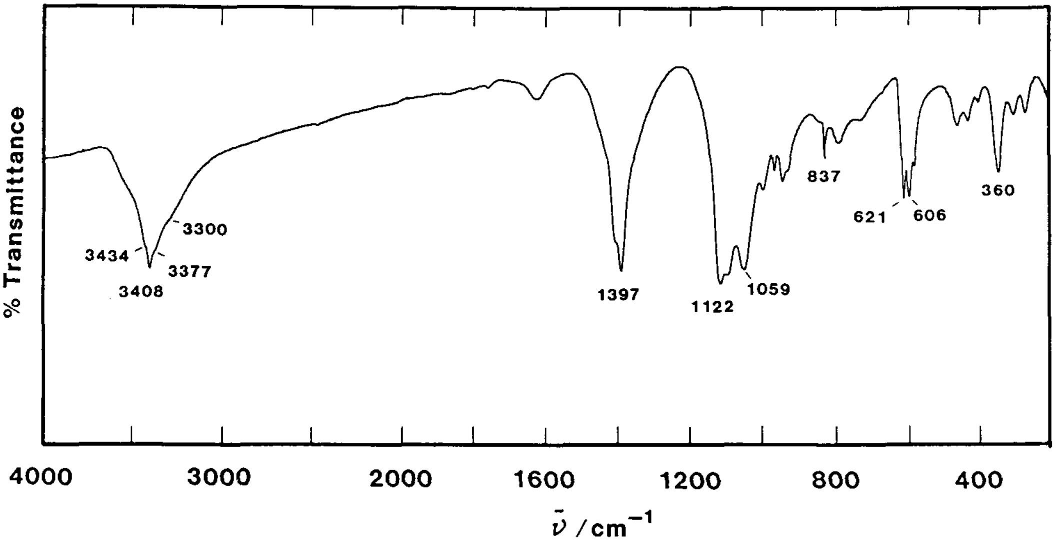

FIG. 1. Infra-red spectrum of caledonite. 0.8 mg in 13 mm diameter CsI disc, recorded on Perkin Elmer 580B instrument.

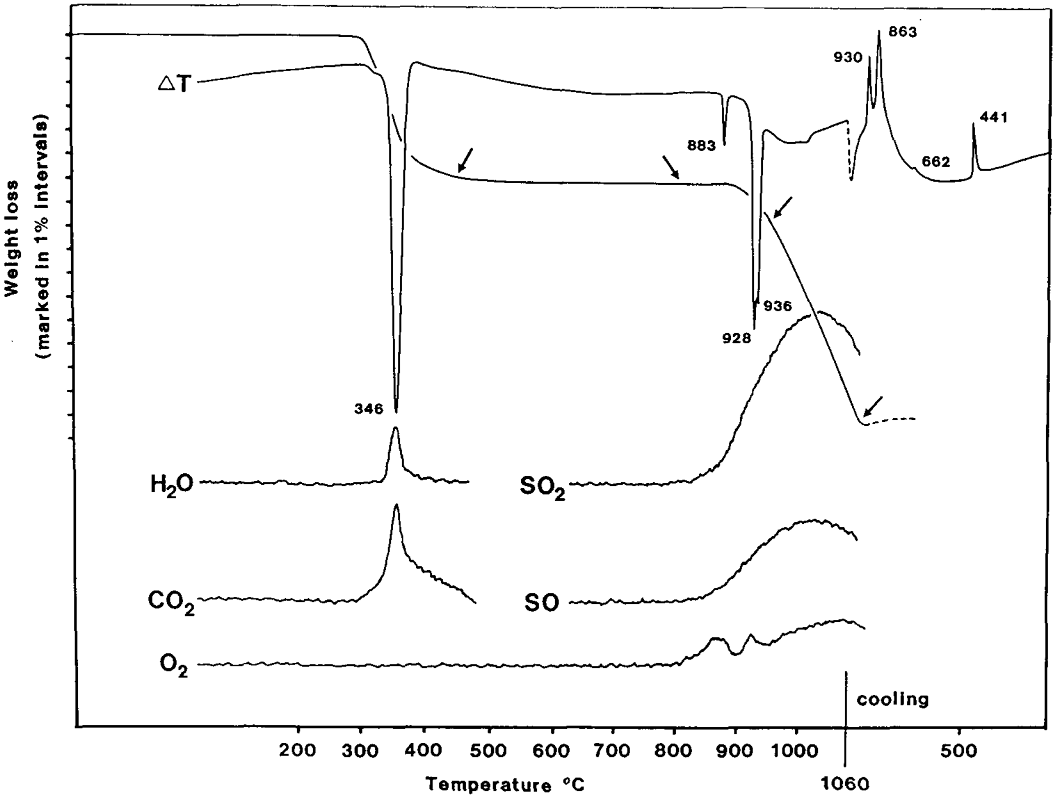

FIG. 2. DTA, TG, and volatile evolution profiles for caledonite. 30 mg sample in flowing nitrogen. Heating rate 15 °C/min to 1060 °C; natural cooling rate.

TABLE I. Phases identified in products cooled from different temperatures on the caledonite DTA curve (see Fig. 2).

$^{\circ}$C	CuO	Cu_2O	$PbSO_4$	$PbO.PbSO_4$	β-$2PbO.PbSO_4$	$4PbO.PbSO_4$
550	o	o	●	●*		
800	o	o	●	●*		
950	o	o		●		
1060	o	o			●	o

● major (* dominant)

o minor

Methods

Simultaneous DTA-TG curves and volatile evolution profiles were obtained in flowing nitrogen and at a heating rate of 15 °C/min, using a Stanton Redcroft STA 781 thermal analyser linked to a quadrupole mass spectrometer. Sample weights varied between 20 and 50 mg. Interfacing between the thermal analyser and the mass spectrometer was by an inert glass-lined capillary which was heated to avoid condensation.

X-ray studies on intermediate decomposition products were made on spindle mounts in a 114.6 mm diameter Debye-Scherrer powder camera using Cu-Kα radiation.

Results and discussion

Simultaneous DTA-TG curves are given in fig. 2, together with evolution profiles for H_2O, CO_2, O_2, SO_2, and SO. Phases identified in products cooled from intermediate temperatures indicated on the DTA curve are recorded in Table I.

Reactions 20–800 °C. Water and CO_2 are expelled in a single sharp endothermic reaction with a peak at 346 °C on the DTA curve. The temperature of this peak was unaffected by P_{CO_2} up to 1 atmosphere (cf. the behaviour of basic copper carbonate described by Henmi *et al.*, 1985). The weight loss corresponding to this endothermic reaction is 6.2 % (theoretical $H_2O + CO_2$ content of caledonite = 6.08 %). In contrast to that of H_2O, the CO_2 profile shows a marked 'tailing off' towards higher temperatures and the TG curve does not plateau until 640 °C. X-ray powder photographs of products heated to 550 and 800 °C were virtually identical (Table I), these indicating major $PbO \cdot PbSO_4$, significant $PbSO_4$, and minor CuO and Cu_2O. Both CuO and Cu_2O lines were slightly stronger in the product from 800 °C but no copper sulphate lines were detected in either powder photograph.

This initial decomposition can be represented by:

$$Pb_5Cu_2(SO_4)_3(CO_3)(OH)_6 \rightarrow 2[PbO \cdot PbSO_4] + PbSO_4 + 2CuO + CO_2 + 3H_2O. \quad (1)$$

This agrees with the above observations except that it does not take account of the identification of Cu_2O in the decomposition products. Copper is present as Cu(II) in the caledonite structure, each Cu atom occurring in pseudo-octahedral sites surrounded by 4OH and 2O (Giacovazzo *et al.*, 1973). The occurrence of both CuO and Cu_2O in the decomposition residue is therefore anomalous as there does not appear to be any scope for reduction of Cu(II) during decomposition by any other products of the reaction. In addition, no oxygen was liberated during this reaction (see O_2 trace on fig. 2). However, in order to accommodate the X-ray identification of both CuO and Cu_2O as reaction products, the decomposition may be represented by

$$Pb_5Cu_2(SO_4)_3(CO_3)(OH)_6 \rightarrow 2[PbO \cdot PbSO_4] + PbSO_4 + CuO + \tfrac{1}{2}Cu_2O + \tfrac{1}{2}O + CO_2\uparrow + 3H_2O\uparrow. \quad (2)$$

In this equation the assumption is made that any oxygen liberated is retained within the reaction products; as will be seen from the next section, there is some experimental evidence for this.

Reference to the phase diagram for the system PbO–$PbSO_4$ shows that the lead sulphate/oxysulphate decomposition product plots in a position equivalent to point B in fig. 3.

Reactions 800–1060 °C. The DTA curve in fig. 2 shows three sharp endothermic peaks at 883, 928, and 936 °C. These three temperatures correspond respectively to the α-β $PbSO_4$ transition (point C, fig. 3), the start of incongruent melting of the 2:1 $PbO \cdot PbSO_4$ decomposition mixture (point D), and the formation of a true liquid (point E). Breakdown of the sulphate anion begins at approximately the same temperature as that of the

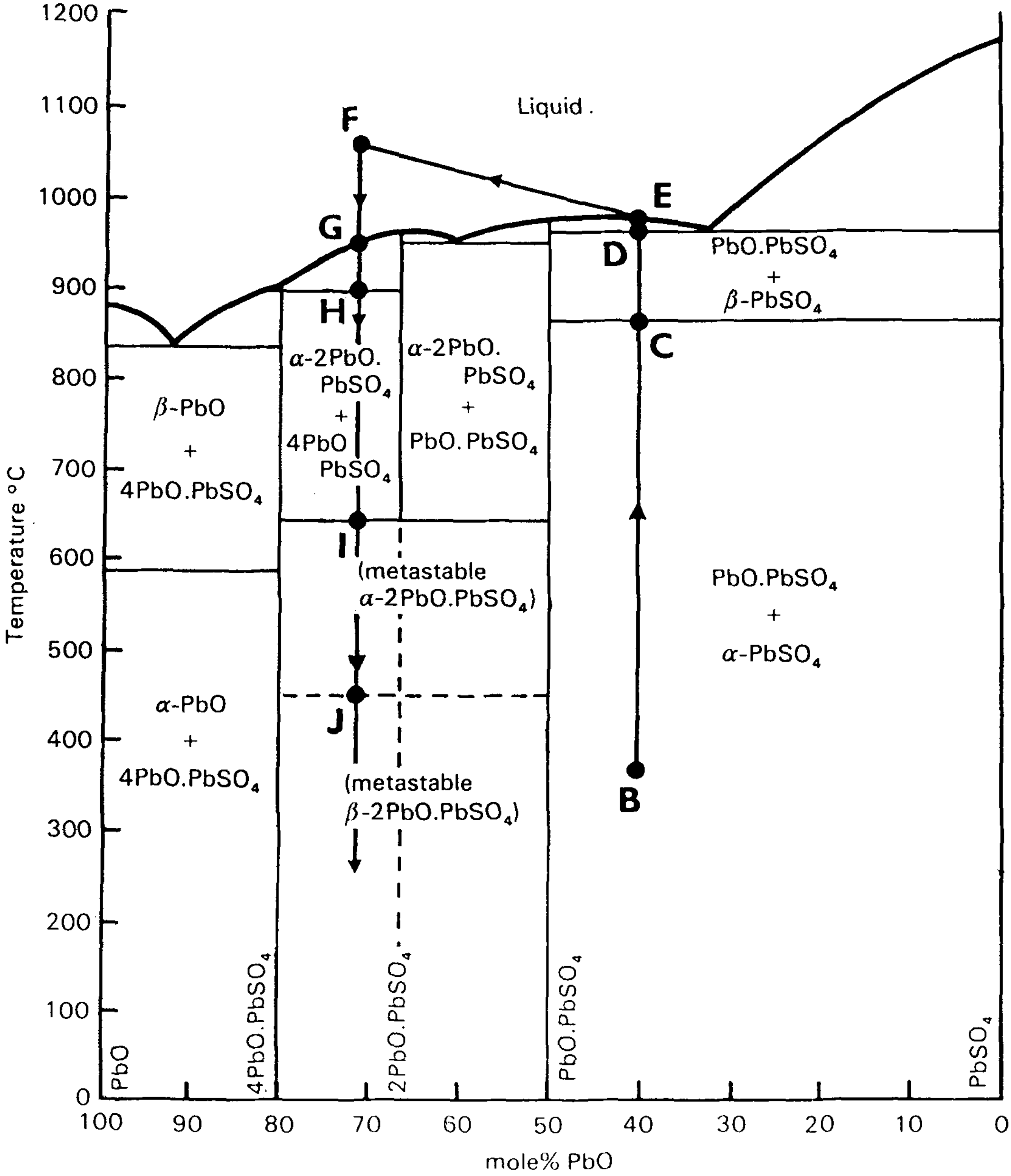

FIG. 3. Phase diagram for the system PbO-$PbSO_4$ (after Billhardt, 1970) showing decomposition route of caledonite. Points B-J are discussed in the text.

α-β $PbSO_4$ transition and appears to be accompanied by evolution of SO_2, SO, and O_2. The evolution profiles of all three volatiles have similar shapes and peak at approximately the same temperatures but the oxygen profile contains two additional peaks, a relatively sharp one at 890 °C and a smaller, less well-defined one at 930 °C. The coincidence of these peaks with those on the DTA curve corresponding to the α-β $PbSO_4$ transition and subsequent melting reactions suggests that they are due to physical release of oxygen which was trapped within the products of the first decomposition. Isolation of decomposition products of other lead minerals by oxysulphate formation has been postulated previously by Gray *et al.* (1967) and Bugajska and Karwan (1979).

The heating programme was stopped at 1050 °C following a weight loss of ~ 10% for this second decomposition reaction. A product cooled from 950 °C, i.e. half-way through the reaction, showed major $PbO \cdot PbSO_4$ and minor CuO and Cu_2O (Table I). The residue from this reaction (1060 °C) showed major $2PbO \cdot PbSO_4$ and minor $4PbO \cdot PbSO_4$, CuO, and Cu_2O. The reaction to 1060 °C could thus be represented in general terms by the equation:

$$\begin{aligned}&6[PbO \cdot PbSO_4] + 3PbSO_4 \rightarrow\\ &\quad 5[2PbO \cdot PbSO_4] + 3SO_2\uparrow + \tfrac{5}{2}O_2\uparrow + SO\uparrow. \qquad (3)\end{aligned}$$

This takes account of the relative ratios of SO_2 to SO evolved and also the fact that $2PbO \cdot PbSO_4$ was the dominant lead oxysulphate phase identified in the residue; the theoretical weight loss for this reaction is 10.1%. However, equation (3) can only be an approximation of the process as (i) $4PbO \cdot PbSO_4$ was identified as a minor phase in the residue; (ii) although primarily due to breakdown of the sulphate anion, this second weight loss must have involved some evaporation of PbO also, as yellow deposits were noted in the furnace and gas line at the end of the run; (iii) a thermal reaction yielding $SO_2 + SO + O_2$ simultaneously seems thermodynamically unlikely.

With regard to point (iii) above, there is some controversy over the exact species evolved during thermal decomposition of the sulphate anion, which has arisen both because of the temperature-dependent dissociation $SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$ (Stern and Weise, 1966) and differences in experimental conditions under which the thermal decomposition has been investigated. Truex *et al.* (1977) studied the decomposition of aluminium sulphate in a flow reactor system in the range 500–700 °C. They found that SO_3 comprised 97% of the emitted sulphur oxides; the small amount of SO_2 identified was attributed to the extremely short residence time of the SO_3 in the system (1 sec) before collection, which thus minimized the $SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$ dissociation. Collins *et al.* (1974), using mass spectrometry, showed that for anhydrous $CuSO_4$ and $Al_2(SO_4)_3$, SO_3 was the initial gaseous decomposition product. The SO_3 dissociated to SO_2 and O_2; SO also appeared on the mass spectra due to the dissociation $SO_2 \rightarrow SO^+ + O^-$ within the ionization chamber of the mass spectrometer. No SO_3 was detected in mass spectra of gases evolved from alunite, however, and it was suggested by Collins *et al.* that SO_2 and SO were primary products of the decomposition of this mineral. Lombardi (1984) figured mass spectra of the gaseous decomposition products of three alunites which showed SO_3, SO_2, and SO, but in widely differing ratios. SO is a thermodynamically unstable, fugitive species with a lifetime of a fraction of a second, and is unlikely to survive the journey from sample to mass spectrometer (see e.g. Greenwood and Earnshaw, 1984). Therefore, the most likely explanation for its presence on mass spectra of sulphate decomposition products is that it is a fragment ion of the decomposition of SO_2 within the mass spectrometer. This would explain the similarity between SO and SO_2 profiles in fig. 2 (see also Lombardi, 1984, fig. 5). Equation (3) can thus be modified as follows:

$$\begin{array}{rl}
6[PbO \cdot PbSO_4] + 3PbSO_4 \rightarrow & \\
5[2PbO \cdot PbSO_4] + & 4SO_3 \\
\text{dissociation} > 800\ ^\circ\text{C} & \Big\downarrow \\
 & 4SO_2 + 2O_2 \\
\text{partial dissociation in mass spectrometer} & \Big\downarrow \\
 & 4SO^+ + 4O^-. \qquad (4)
\end{array}$$

The result of this second decomposition to 1060 °C was to increase the amount of PbO relative to $PbSO_4$ in the decomposition residue, as shown by the line E–F in fig. 3. The position of point F is only approximate, but can be justified by reactions undergone by the residue on cooling (see next section).

Reactions on cooling from 1060 °C. Major $2PbO \cdot PbSO_4$ and minor $4PbO \cdot PbSO_4$ were identified in the residue cooled from 1060 °C. On the phase diagram in fig. 3, this would place its composition just to the left of the vertical composition line $2PbO \cdot PbSO_4$, i.e. point F (at a temperature of 1060 °C). All the peaks on the DTA cooling curve agree with this positioning. The peak at 930 °C represents the transition from true to incongruent melt (point G) and that at 863 °C the transition from incongruent melt to solid (point H). A very small peak at 662 °C could be due to minor decomposition of α-$2PbO \cdot PbSO_4$ into $PbO \cdot PbSO_4$ and $4PbO \cdot PbSO_4$ (point I; see also Billhardt, 1970), but the bulk of the α-$2PbO \cdot PbSO_4$ changes to the β-form, as represented by the peak at 447 °C (point J).

Summary and conclusions

On heating, caledonite decomposes between 300 and 400 °C to give a mixture of $PbO \cdot PbSO_4$, $PbSO_4$, and Cu(II) and Cu(I) oxides. CO_2 and hydroxyl water are liberated during this reaction; some oxygen also appears to be generated but is not physically released from the decomposition residue until higher temperatures are attained.

Subsequent reactions undergone by the decomposition residue are governed only by the nature of the lead sulphate and oxysulphate components, with temperatures for phase transition and melting reactions agreeing well with those predicted from the PbO-$PbSO_4$ phase diagram. Breakdown of the sulphate anion commences at 880 °C with SO_2, SO, and O_2 appearing on the mass spectra of the decomposition products. The initial gaseous decomposition product was probably SO_3, which dissociated completely to SO_2 and O_2 at these high temperatures. The SO is an artefact arising from partial fragmentation of SO_2 within the mass spectrometer. Above 1000 °C, some evaporation of PbO occurs but CuO and Cu_2O are still present in products cooled from 1060 °C.

Whilst linking evolved gas detectors to DTA-TG equipment is by no means a new technique in mineral thermal analysis, the present investigation has confirmed both the need for this approach when dealing with minerals showing complex volatile evolution behaviour and also the flexibility afforded by the quadrupole mass spectrometer compared to a system employing separate detectors for each volatile (cf. Morgan, 1977; Milodowski and Morgan, 1984).

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