

Thermal behavior of valleriite

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Abstract

The thermal decomposition process of a valleriite from Kaveltorp (Sweden) in oxidant and inert atmosphere is studied, to establish new data about its stability conditions. Interpretation of the ATD and TG curves is also made, taking into account the products obtained.

Introduction

According to Evans and Allman (1968), valleriite is a Fe-Cu sulphide with a "hybrid" structure, which consists of alternating brucite-like and sulphide layers. The sulphide layers consist of two sheets of sulphur atoms in close-packed association, with all of the tetrahedral sites occupied at random by Fe and Cu atoms; in the brucite-like layers, Fe and Al can substitute for Mg, and Al for Mg can be present. Yund and Kullerud (1966) and Iiishi *et al.* (1970) have studied the stability of valleriite. Data on the thermal decomposition of this mineral are given by Harris and Vaughan (1972) and Harado *et al.* (1973). This study concerns the thermal behavior of valleriite in oxidizing and inert atmospheres, at atmospheric pressure. From the results, the combustion heat of this mineral has been determined.

Apparatus and material

The thermal analyses were carried out with Delta-therm apparatus, models D-2000 and D-4000. The working conditions were as follows: thermocouples of Pt-PtRh, heating rate 10°C/min., sample weight 10 mg (diluted with 20% of alumina) for differential thermal analysis (DTA) and 2-4 mg for thermogravimetric analysis (TGA), both a static air atmosphere and a dynamic N₂ atmosphere for DTA and static N₂ atmosphere for TGA. X-ray diffraction analyses were carried out with a Philips diffractometer, model PW-1130-1050-1051, using Ni-filtered CuK radiation. The results were compared with the corresponding ASTM fiches. The valleriite sample studied is from Kaveltorp, Sweden, and was donated by the Riksmuseum of Stockholm. This sample contains about 6 percent calcite, determined by X-ray diffraction, according to the method proposed by Ayllon *et al.* (1975). Ac-

ording to Evans and Allman (1968) the chemical composition of this valleriite is approximatively:



Experimental results

In an oxidizing atmosphere in the range 20-250°C valleriite is stable (Fig. 1a). At 250°C a complex combustion process begins, which appears as a change of slope in the DTA curve, and which culminates in a large exothermic effect at 431°C and a small one at 486°C. At 832°C an asymmetric endothermic effect occurs.

The TGA curve (Fig. 1b) shows a continuous weight increase resulting from the oxidation of sulphide to sulphates (a total increase of 41.74%) until 650°C. Between 650°C and 943°C a weight loss of 56.82 percent is observed; thus the final weight is 15.08 percent less than the initial weight at 25°C.

The X-ray diffraction patterns of the sample, heated at 430°C 600°C and 900°C show that at 430°C, the valleriite disappears, the calcite remains, and copper oxysulphate [Cu₂(SO)₄O], CuO, anhydrite and spinel [Mg(Fe,Al)₂O₄] appear as new phases. At 650°C an increase of the intensity of X-ray diffraction lines corresponding to anhydrite, CuO, and copper oxysulphate is observed, spinel and calcite remain, and magnetite and MgO appear. At 900°C, only anhydrite, magnetite, MgO, and spinel remain.

The combustion heat of valleriite has been calculated following the method proposed by Sabatier (1954) and modified by Bruinj and Van der Marel (1954), calibrating the apparatus with sulphides of known combustion heat. The result obtained is 91.54 kcal/mol.

In an inert atmosphere the DTA curve reveals two

small endothermic effects, one at 490°C and the other at 848°C (Fig. 2). The TGA curve shows a weight loss of 9.20 percent between 350° and 568°C and of 2.44 percent between 800° and 900°C.

The X-ray diffraction patterns observed at temperatures of 450°, 550°, and 1000°C show the following: At 450° no change is observed; at 550°, no valleriite is present, chalcopyrite and spinel appear, and calcite remains; at 1000° the only additional change observed corresponds to the disappearance of calcite.

Discussion

The above results for the thermal decomposition of valleriite in an inert atmosphere show that the dehydroxylation of brucite-like layers starts at about 350°C, followed by the lattice breakdown and the formation of spinel and chalcopyrite as stable phases. This assumption is supported by the first DTA endothermic effect and the first steep rise in the TGA curves. The second steep rise of the TGA curve, as well as the last DTA endothermic effect, must be attributed to decomposition of the calcite present in the sample. The calculated weight loss corresponds to 6 percent calcite, the same quantity determined by X-ray diffraction. The decomposition temperature of valleriite obtained by us does not agree with that found by Harris and Vaughan (1972), who gave it as 114–158°C. In an oxidizing atmosphere, the lattice breakdown is not observed, probably since the oxidation process between 250°C and 650°C masks it. From the initial valleriite and calcite ratios and the phases present at 900°C—CuO, spinel, magnetite, MgO, and anhydrite (from calcite sulphatation)—the calculated weight loss for the process is 15.01 percent which is in agreement with that obtained from the experimental curve (15.08%).

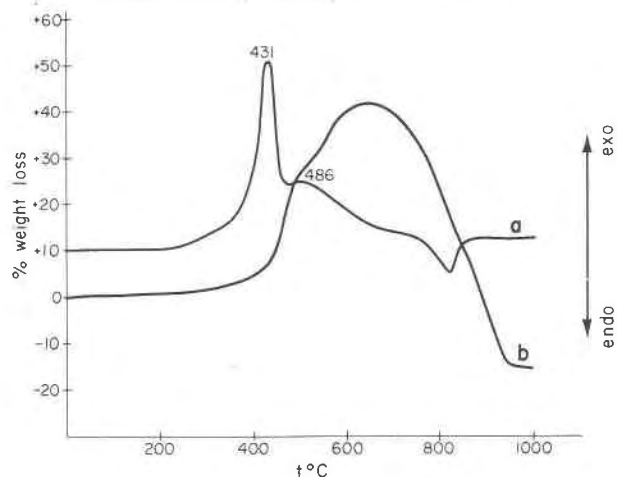


Fig. 1. DTA and TGA curves of valleriite in an oxidizing atmosphere.

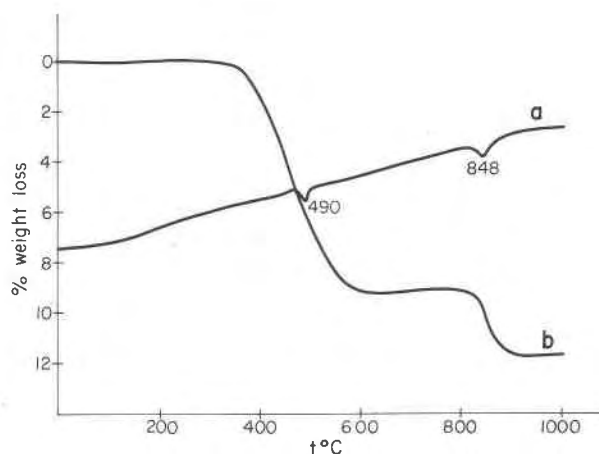
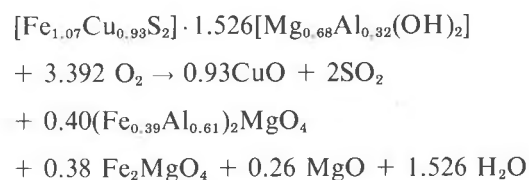


Fig. 2. DTA and TGA curves of valleriite in an inert atmosphere.

Knowing the heat of combustion of valleriite and the chemical composition of the sample, the enthalpy of formation ΔH_f^0 at 704°K, has been calculated from the following possible reaction:



The calculated values, -651.5 kcal/mol, are considerably smaller than those of sulphides which do not have brucite-like layers in their structures, which means that this mineral is less stable than those.

References

- Ayllon, M., A. La Iglesia and J. M. Martín Pozas (1975) Quantitative analysis by X-ray diffraction of some accessory clay minerals using a method of internal standard. *Collected Abstr. Tenth Int. Congr. Crystallogr.*, Amsterdam, 5–201.
- Bruijn, C. M. A. and H. W. Van der Marel (1954) Mineralogical analysis of soil clays: I, Introduction and differential thermal analysis. *Geol. Mijnbouwkde*, 16, 69–83.
- Evans, H. T. Jr. and R. Allman (1968) The crystal structure and crystal chemistry of valleriite. *Z. Kristallogr.*, 127, 73–93.
- Harado, K., K. Nakao and K. Nagashima (1973) Valleriite from Little chief Mine, White Horse copper belt, Yukon. *Can. Mineral.*, 7, 1037–1052.
- Harris, D. C. and D. J. Vaughan (1972) Two fibrous iron sulphides and valleriite from Cyprus with new data on valleriite. *Am. Mineral.*, 57, 1037–1052.
- Iiishi, K., T. Tomisaka, T. Kato and S. Takeno (1970) Synthesis of valleriite. *Am. Mineral.*, 55, 2107–2110.
- Sabatier, G. (1954) La mesure des chaleurs de transformations à l'aide de l'analyse thermique différentielle. *Bull. Soc. fr. Mineral. Cristallogr.*, 77, 935–968, 1077–1083.
- Yund, R. A. and G. Kullerud (1966) Thermal stability assemblages in the Cu–Fe–S system. *J. Petrol.*, 7, 454–488.