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THERMAL ANALYSIS OF BEAVERITE IN COMPARISON WITH PLUMBOJAROSITE

R. L. Frost[*], *A. J. Locke and W. Martens*

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology
GPO Box 2434, Brisbane Queensland 4001, Australia

The thermal decomposition of beaverite and plumbojarosite was studied using a combination of thermogravimetric analysis coupled to a mass spectrometer.

The mineral beaverite $Pb(Fe,Cu)_3(SO_4)_2(OH)_6$ decomposes in three stages attributed to dehydroxylation, loss of sulphate and loss of oxygen, which take place at 376 and 420, 539 and 844°C. In comparison three thermal decomposition steps are observed for plumbojarosite $PbFe_6(SO_4)_4(OH)_{12}$ at 376, 420 and 502°C attributed to dehydroxylation; loss of sulphate occurs at 599°C; and loss of oxygen and formation of lead occurs at 844 and 953°C. The temperatures of the thermal decomposition of the natural plumbojarosite were found to be less than that for the synthetic jarosite. A comparison of the thermal decomposition of plumbojarosite with argentojarosite is made. The understanding of the chemistry of the thermal decomposition of minerals such as beaverite, argentojarosite and plumbojarosite and related minerals is of vital importance in the study known as 'archeochemistry'.

Keywords: *argentojarosite, beaverite, dehydration, dehydroxylation, plumbojarosite, TG*

Introduction

The mineral beaverite $[Pb(Fe,Cu)_3(SO_4)_2(OH)_6]$ is one mineral of the many jarosite minerals [1] and was first discovered in 1911 [2]. Beaverite is like plumbojarosite in that it forms in close proximity to Fe–Pb–Cu sulphides [1, 3]. The mineral is related to jarosites and alunites and is trigonal. Beaverite forms a solid solution with plumbojarosite with replacement of the Fe^{3+} by Cu^{2+} or Zn^{2+} or both [4]. Beaverite is related to the mineral plumbojarosite. Lead jarosite (plumbojarosite) $(PbFe_6(SO_4)_4(OH)_{12})$ was identified in relation to jarosite in 1902 [5]. Plumbojarosite is often found in cationic mixed jarosites [6–15]. Such minerals are of importance in medieval and archaeological science [16, 17]. The minerals are found in mine drainage sites both ancient and modern [9, 17, 18]. Such formation of jarosites has been occurring since before the Bronze Age [19]. The importance of jarosite formation and its decomposition depends upon its presence in soils, sediments and evaporate deposits [20]. These types of deposits have formed in acid soils where the pH is less than pH 3.0 units [21].

The thermal decomposition of jarosites has been studied for some considerable time [22–26]. The authors have reported recent studies of jarosites both natural and synthetic [10–15]. There have been many studies on related minerals such as the Fe(II) and Fe(III) sulphate minerals [27–32]. Interest in such minerals and their thermal stability rests with the possible identification of these minerals and related dehydrated paragenetically related minerals on planets and on Mars. The existence of these minerals on planets would positively identify existence or at least pre-existence of water on Mars [33]. Further such minerals are formed through crystallisation from solutions. It has been stated that the thermal decomposition of jarosite begins at 400°C with the loss of water [34]. The process is apparently kinetically driven. Water loss can occur at low temperatures over extended periods of time [34]. It is probable that in nature low temperature environments would result in the decomposition of jarosite. The products of the decomposition depend upon the jarosite be it K, Na or Pb, etc. but normally goethite and hematite are formed together with soluble sulphates [35]. Recently thermogravimetric analysis has been applied to some complex mineral systems and it is considered that TG-MS analyses may also be applicable to the jarosite minerals [36–41]. Differential thermal analysis of some related minerals has been published [24, 42–44]. In this work we report the thermogravimetric analysis of beaverite and make a comparison with plumbojarosite.

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[*] Author for correspondence: r.frost@qut.edu.au

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

Minerals

The mineral beaverite was synthesised according to the method given by Jambor and Dutrizac [45]. A 40 mL chloride solution was prepared. It contained 0.25 g $PbCl_2$, 5 mL of 1.23 M $FeCl_3$ and 12 mL of saturated LiCl solution with the remaining volume being water. A separate sulphate solution was also prepared. This contained 2.5 g $Fe_2(SO_4)_3$ and 4.62 g $CuSO_4$ dissolved in a minimal volume of water. The sulphate solution was added dropwise to the chloride solution over a 5 min time period. The solution was transferred to an autoclave and enough water was added to bring the final volume of the solution to approximately 0.1 L. The autoclave was heated at 120°C for 3 days. After this time, the brown precipitate was collected, washed and dried under vacuum. 1.33 g of sample was obtained and identified by X-ray diffraction as beaverite.

The mineral plumbojarosite has been synthesized by the authors [10]. Natural plumbojarosite originated from Teutonic Bore Mine, Western Australia. The beaverite and plumbojarosite were analysed by X-ray diffraction for phase purity and by electron probe using energy dispersive techniques for quantitative chemical composition. Natural plumbojarosite contained 5% potassium. No other cations were found.

Methods

X-ray diffraction

XRD analyses were performed on a PANalytical X'Pert PRO X-ray diffractometer (radius: 240.0 mm). Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 45 kV and 35 mA, providing $K\alpha_1$wavelength of 1.540596 Å. The incident beam passed through a 0.04 rad, Soller slit, a 1/2° divergence slit, a 15 mm fixed mask and a 1° fixed anti-scatter slit. After interaction with the sample, the diffracted beam was detected by an X'Celerator RTMS detector. The detector was set in scanning mode, with an active length of 2.022 mm. Samples were analysed utilising Bragg–Brentano geometry over a range of 3–75° 2θ with a step size of 0.02° 2θ, with each step measured for 200 s.

Thermal analysis

Thermal decomposition of beaverite and plumbojarosite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (60 cm^3 min^{-1}). Approximately 35 mg of sample underwent thermal analysis, with a heating rate of 5°C min^{-1}, with high resolution, to 1000°C. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only water vapour, carbon dioxide and oxygen were analyzed. Previous studies by the authors have reported these experimental methods [10–14].

Results and discussion

The XRD pattern of beaverite and the reference pattern are shown in Fig. 1. The synthesised mineral shows an XRD pattern identical to that of the standard. Some sulphates of lead and copper are present as impurities but are estimated to be in low concentrations. and Dutrizac showed that substitution of Pb^{2+} by Cu^{2+} results in the formation of a probable solid solution series between beaverite and plumbojarosite [4]. The authors discussed the lack of studies on this topic and the lack of fundamental knowledge of such minerals and on their solid solutions [4].

TG and DTG curves for beaverite are shown in Fig. 2 and the mass spectrometric ion current curves in Fig. 3. The ion current curves are shown for mass/charge ratios of 44, 17, 18, 16, 32, 48 and 64 repre-

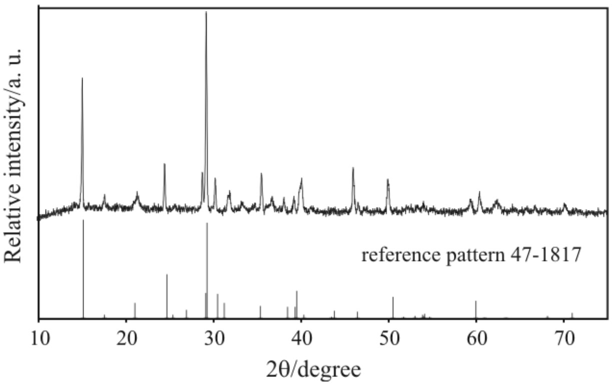

Fig. 1 XRD pattern of beaverite

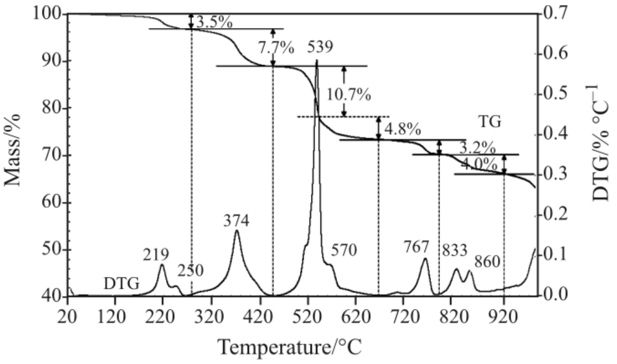

Fig. 2 TG and DTG curves of beaverite

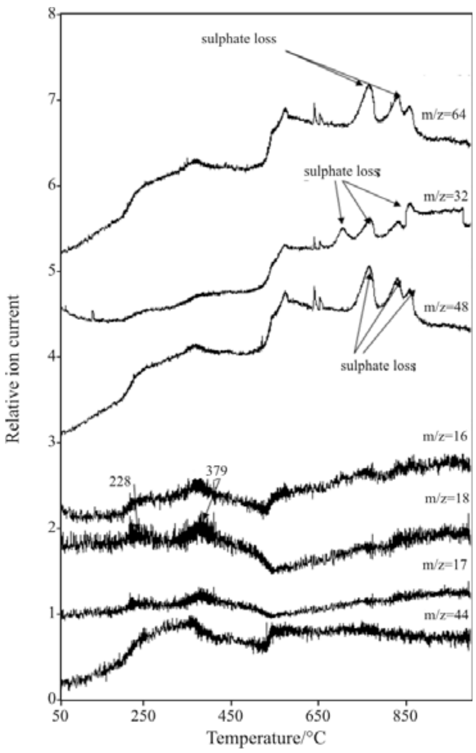

Fig. 3 Ion current curves of the evolved gases from the thermal decomposition of beaverite

senting the gas evolution attributed to CO_2, OH, H_2O, O, O_2, SO_2 and SO_3. M/z ratio of 44 is analysed to check to see if any CO_2 is involved with the combustion and thermal decomposition of the beaverite.

Mechanism of thermal decomposition of beaverite

It is proposed that the thermal decomposition of beaverite $[Pb(Fe,Cu)_3(SO_4)_2(OH)_6]$ occurs in three stages as follows: (a) dehydroxylation, (b) loss of sulphate, (c) loss of oxygen.

Stage 1 Temperatures of 219, 250 and 374°C

$$[Pb(Fe,Cu)_3(SO_4)_2(OH)_6]\rightarrow$$
$$[Pb\ (Fe,Cu)_3O_3(SO_4)_2]+3H_2O$$

Theoretical mass loss of 9.56% is predicted.

Experimental mass losses of 3.5% at 219 and 250°C are observed. A further mass loss attributed to dehydroxylation of 7.7% at 374°C is found.

The total mass loss for dehydroxylation of 11.2% is observed.

Ion current curves show gas evolution of water at 228 and 379°C which corresponds to the mass losses at 219, 250 and 374°C.

Stage 2 Temperatures of 539 and 570°C

$$[Pb(Fe,Cu)_3O_3(SO_4)_2]\rightarrow$$
$$[Pb(Fe,Cu)_3O_7]+2SO_2$$

Theoretical mass loss of 12.68% is predicted.

Experimental mass loss for the synthesised beaverite is 15.5%. In the ion current curves (Fig. 3) mass losses of 32, 48 and 64 corresponding to S, SO and SO_2 are observed.

Stage 3 Temperatures of 767, 833 and 860°C

$$2[Pb(Fe,Cu)_3O_7]\rightarrow$$
$$2Pb+3Fe_2O_3+3CuO+O_2$$

Theoretical mass loss of 5.7%.

Experimental mass loss for the synthesised beaverite is 7.2%. The ion current curves show increased current for m/z=16 at 767, 833 and 860°C.

Mechanism of thermal decomposition of plumbojarosite

Thermogravimetric analysis

The TG and DTG curves for natural lead jarosite are shown in Fig. 4. The ion current curves for the evolved gases water vapour and SO_2 from the plumbojarosite are shown in Figs 5a and b. There is an apparent lowering of the temperatures of decomposition for the natural plumbojarosite as compared with a synthetic plumbojarosite. This may be caused by the presence of other elements in the natural plumbojarosite. EDX analysis shows the presence of around 5% K in the natural plumbojarosite.

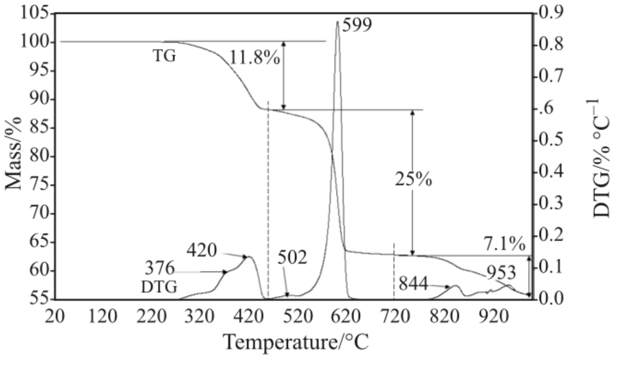

Fig. 4 TG-DTG curves of Pb-jarosite

The ion current curves for evolved water vapour show water is evolved over a broad temperature range from 350 to 450°C. Mass losses that occur at 376, 420 and 502°C for the synthetic plumbojarosite and 391 and 418°C for the natural sample are attributed to dehydroxylation. The theoretical mass loss for dehydroxylation is 9.56% based upon the formula $(PbFe_6(SO_4)_4(OH)_{12})$ with the loss of

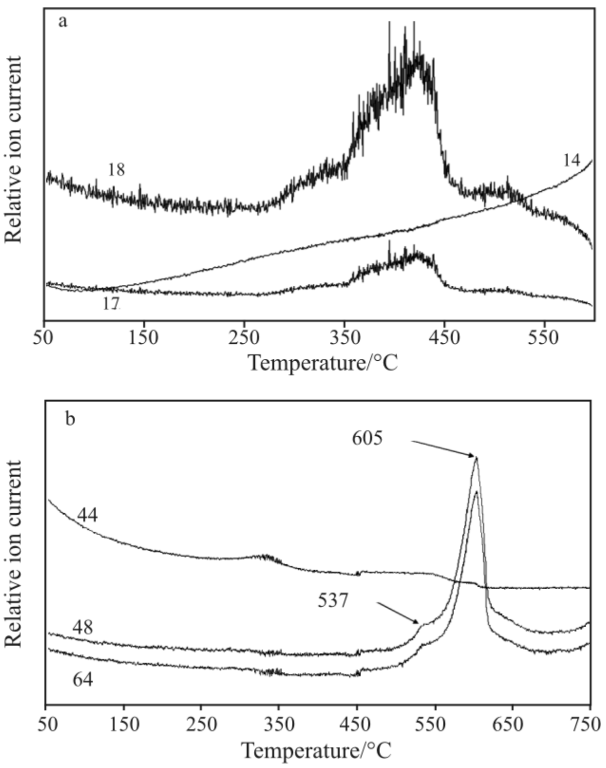

Fig. 5 Ion current curves of a – m/z=17 and 18; b – m/z=44, 48 and 64 for plumbojarosite as a function of temperature

6 hydroxyl units as $3H_2O$. The experimentally determined mass losses for synthetic and natural plumbojarosites are 11.8 and 11.2%.

The ion current curve for evolved SO_2 (Fig. 5b) shows that the mass loss for the synthetic plumbojarosite at 605°C is due to the loss of sulphate as SO_2. The temperature for the natural plumbojarosite is 531°C. The difference in temperature is attributed to a 'depression of freezing point effect' i.e. a lowering of the temperature of the loss of sulphate by the presence of impurities in the natural sample. The experimental mass loss is 25%. If all 4 sulphate units are lost simultaneously then the theoretical mass loss would be 22.68%. Higher temperature mass losses are observed at 953 and 844°C for plumbojarosite and at 812 and 759°C for the natural sample. These mass loss steps are attributed to the loss of oxygen. XRD shows the decomposition products of plumbojarosite are lead and hematite.

Mechanism of thermal decomposition

It is proposed that the thermal decomposition of plumbojarosite occurs in three stages as follows: (a) dehydroxylation, (b) loss of sulphates, (c) loss of oxygen.

Stage 1

$$PbFe_6(SO_4)_4(OH)_{12}\rightarrow PbFe_6(SO_4)_4O_6+3H_2O$$

Theoretical mass loss of 9.56%.
Experimental mass loss is 11.8%.
Temperature of mass loss occurs at 376 and 420°C.

Stage 2

$$Pb(FeO)_6(SO_4)_4\rightarrow PbO_{10}(FeO)_6+4SO_2$$

Theoretical mass loss of 22.68%.
Experimental mass loss for the synthesised Plumbojarosite is 25%.
Temperature of mass loss is 599°C.

Stage 3

$$PbO_{10}(FeO)_6\rightarrow Pb+3Fe_2O_3+3.5O_2$$

Theoretical mass loss of 5.7%.
Experimental mass loss for the Pb-jarosite is 5.6%.
Temperature of mass loss is 844 and 953°C.

Karoleva *et al.* reported the DTA patterns for a number of jarosites and suggested that the sublimation of lead may be a problem in the thermal analysis of lead jarosite [46]. There is a mass loss around 1000°C which may be ascribed to the lead sublimation. Only single endothermic peaks were observed by these authors. In comparison the TG patterns of plumbojarosite show a considerable number of thermal decomposition steps. Kulp and Adler reported similar DTA results [23]. Ozacar *et al.* researched the kinetics of the thermal decomposition of plumbojarosite and basically stated there were three decomposition stages (a) up to 760°C, (b) up to 1000 and up to 1250°C. Such a study does not differentiate between the chemical processes of dehydroxylation and desulphation of the plumbojarosite. There have been no reported fundamental studies of the TG and TG-MS of plumbojarosite and beaverite.

Comparison with the thermal decomposition of argentojarosite

To date there have been few studies of the thermal decomposition of argentojarosite [12]. The thermal decomposition of argentojarosite takes place with steps similar to that for beaverite and plumbojarosite. Dehydroxylation of argentojarosite occurs in three stages at 228, 383, 463°C with the loss of 2, 3 and 1 hydroxyl units. Loss of sulphate occurs at 548°C and is associated with a loss of oxygen. At 790°C loss of oxygen only leaves metallic silver and hematite.

Thermal decomposition of argentojarosite is important in understanding silver production in ancient and medieval times. This work shows that temperatures of around 750°C are required to produce metallic silver. Argentojarosite was exploited at Rio Tinto, Spain from Roman and even pre-Roman times for silver production [45]. Argentojarosite had an important influence on the accumulation of wealth of both Europe and South America [45]. Thermal analysis shows the relatively low temperatures at which argentojarosite can be converted to metallic silver. The existence of large quantities of argentojarosite and argento-plumbojarosite resulted in the formation of large quantities of metallic silver.

Conclusions

The thermal decomposition of a natural and synthetic plumbojarosite has been studied using thermogravimetric analysis and mass spectrometry and the thermal decomposition compared with that of beaverite. The temperatures of the thermal decomposition of the natural plumbojarosite were found to be less than that for the synthetic plumbojarosite. This is attributed to a depression of freezing point effect induced by impurities in the natural jarosite. The implication is that lead would be more easily obtained from the plumbojarosite if the mineral was impure which is more often the case than not.

Understanding the chemistry of plumbojarosite and argento-plumbojarosite is of importance in archeochemistry. Plumbojarosite was a source of lead in pre- and Roman times. Argento-plumbojarosite was the major source of silver. It has been stated that much of the wealth of colonial Spain originated from the obtaining of silver from silver containing jarosites. Indeed the wealth of South American civilisations depended on silver. Such lead and silver could only be formed by heating the plumbojarosite and argento-plumbojarosite. For the understanding of the archeochemistry of jarosites it is important to undertake thermal studies of these minerals. Thermal studies provide an indication of the temperatures that ancient civilisations would need to achieve in order to obtain lead and or silver.

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