

Thermal decomposition of jarosites of potassium, sodium and lead

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Abstract

Jarosites are a group of minerals formed in evaporite deposits and form a component of efflorescence. As such the minerals can function as cation and heavy metal collectors. Thermogravimetry coupled to mass spectrometry has been used to study three Australian jarosites which are predominantly K, Na and Pb jarosites. Mass loss steps of K jarosite occur over the 130 to 330 and 500 to 622 °C temperature range and are attributed to dehydroxylation and desulphation. In contrast the behaviour of the thermal decomposition of Na-jarosite shows three mass loss steps at 215 to 230, 316 to 352 and 555 to 595 °C. The first mass loss step for Na-jarosite is attributed to deprotonation. For Pb-jarosite two mass loss steps associated with dehydroxylation are observed at 390 and 418 °C and a third mass loss step at 531 °C is attributed to the loss of SO₃. Thermal analysis is an excellent technique for the study of jarosites. The analysis depends heavily on the actual composition of the jarosite.

Keywords: jarosite, dehydration, dehydroxylation, Raman spectroscopy, high-resolution thermogravimetric analysis

Introduction

The jarosite mineral group has been extensively studied [1]. Jarosite was first discovered on Earth in 1852 in ravines in the mountainous coast of southeastern Spain. The importance of jarosite formation and its decomposition depends upon its presence in soils, sediments and evaporate deposits [2]. These types of deposits have formed in acid soils where the pH is less than 3.0 pH units [3]. Such acidification results from the oxidation of pyrite which may be from bacterial action or through air-oxidation. The Mars mission rover known as opportunity has been used to discover the presence of jarosite on Mars, thus providing evidence for the existence or pre-existence of water on Mars.

<http://www.news.cornell.edu/releases/rover/Mars.jarosite.html>

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The thermal decomposition of jarosites has been studied for some considerable time [4-8]. There have been many studies on related minerals such as the Fe(II) and Fe(III) sulphate minerals [9-14]. Interest in such minerals and their thermal stability rests with the possible identification of these minerals and related dehydrated paragenetically related mineral on planets and on Mars. The existence of these minerals on planets would give a positive indication of the existence or at least pre-existence of water on Mars. 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 [1]. The process is apparently kinetically driven. Water loss can occur at low temperatures over extended periods of time [1]. 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 [15]. Recently thermogravimetric analysis has been applied to some complex mineral systems and the it is considered that TG-MS analyses may also be applicable to the jarosite minerals [16-21]. In this work we report the thermogravimetric analysis of three Australian jarosites.

Experimental

Minerals

The K-jarosite and Na-jarosite originated from Kanmantoo, Mt Lofty Ranges, South Australia; the Pb jarosite from Teutonic Bore Mine, Western Australia. The jarosite minerals were analysed by X-ray diffraction for phase purity and by electron probe using energy dispersive techniques for quantitative chemical composition. The Na-jarosite was found to contain some K and the Pb-jarosite some K as well but at low concentration levels.

Thermal Analysis

Thermal decomposition of the jarosite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm³/min). 34.4 mg of sample underwent thermal analysis, with a heating rate of 5°C/min, resolution of 6°C, to 1000°C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only water vapour, carbon dioxide and oxygen were analyzed.

Results and discussion

Thermogravimetric Analysis and Mass spectrometric analysis

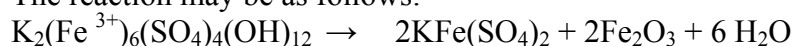
K-Jarosite

The thermal analysis of K-jarosite is shown in **Figure 1**. This figure shows the Thermogravimetric curve and the differential Thermogravimetric curve for K-jarosite.

This figure shows an extended mass loss over the 130 to 330 °C temperature range. A succession of mass loss steps are observed at 501, 556, 598 and 622 °C. The ion current curve for evolved gases is shown in [Figure 2](#). This figure shows that water vapour is the evolved gas over the 130 to 330 °C temperature range. The sum of the MS curves follows the DTG curve precisely. The mass loss steps in the 500 to 622 °C temperature range are attributed to the loss of sulphur dioxide.

Based upon the formula $K_2(Fe^{3+})_6(SO_4)_4(OH)_{12}$ The theoretical mass loss due to the dehydroxylation is 20.35 %. The experimentally determined mass loss was 21.0%.

The reaction may be as follows:



The results for this natural jarosite differ from published results [22]. Drouet and Navrotsky published a thermogravimetric analysis of a synthetic jarosite together with a DSC curve. A mass loss of 3 % was found at 200 °C and was attributed to dehydroxylation. A second mass loss of 12 % was observed for jarosite at a temperature slightly less than 450 °C. A more significant mass loss was found over an extended temperature range from 600 to 800 °C with a mass loss of 23 %. It is readily apparent that the experimental mass loss at 200 °C does not correspond with the expected mass loss due to dehydroxylation of 20.35 %. Even if the second mass loss step of 12 % is ascribed to dehydroxylation, the value is far too low. It should be noted that in this work the rate of heating was very high for careful experimentation. Such experiments are very dependent upon the apparatus and experimental conditions. Some DTA experiments of jarosite showed that the decomposition took place in two steps at 200 and 500 °C with the loss of SO₂ at the latter temperature [5]. Further studies showed that there were five or six exothermic and two endothermic peaks depending upon the cation present in the jarosite [23]. Other earlier studies have shown the dependence of the decomposition of the jarosite on composition [24]. The results of the thermogravimetric analysis of jarosite reported here has shown that the jarosite loses its hydroxyl units at around 220 °C. There is no evidence from mass spectrometry that water is evolved at higher temperatures. Minerals usually originate (are formed) at different localities under different conditions. Crystal structures of thus formed minerals may vary. Synthetic analogues are synthesized under laboratory conditions which are mostly different from those in nature. Their crystal structures may be identical but also differ from natural phases. In the case of hydrated minerals, in phases formed under different conditions (various localities, different laboratories and procedures) the hydrogen-bonding network may significantly vary. Thus differences in the thermal analysis patterns may be observed between the published results from synthetic jarosites compared with natural samples.

Na-jarosite

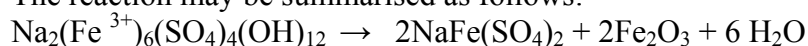
Na-jarosite is of a theoretical formula $Na_2(Fe^{3+})_6(SO_4)_4(OH)_{12}$. Electron probe analysis showed that the Na-jarosite contained some 17 % K. Thus the formula of the Na-jarosite would be better written as $(K_{.17}Na_{.83})_2(Fe^{3+})_6(SO_4)_4(OH)_{12}$.

The thermogravimetric analysis of natural Na-jarosite is shown in [Figure 3](#). Mass loss steps are observed at (a) 215 and 230 °C (b) 316 and 352 °C and (c) 555, 575 and 595 °C. The ion current curves for Na-jarosite shows that water vapour is the evolved gas at the first four temperatures and SO₂ is lost at the three higher temperatures. There is a four percent mass loss due to water loss at 215 and 230 °C. This water may be described as “excess water” [22, 23]. It is possible that this water

results from the deprotonation of the Na-jarosite. Jarosites have a hydroxyl surface which is capable of adsorbing protons creating a hydrogen-jarosite. Thus the Na-jarosite is a sodium protonated jarosites and the formula may be written as $(H_xK_{.17-x/2}Na_{.83-x/2})_2(Fe^{3+})_6(SO_4)_4(OH)_{12}$.

The theoretical mass loss of Na-jarosite based upon the formula $Na_2(Fe^{3+})_6(SO_4)_4(OH)_{12}$ is 11.13 %. If the initial 4 % mass loss is neglected the mass loss at 316 and 352 °C is 10 %. This value is close to the theoretical value.

The reaction may be summarised as follows:

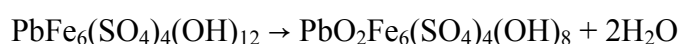


Plumbojarosite

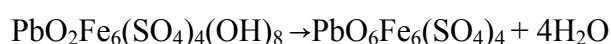
The mineral plumbojarosite is given by the formula $PbFe_6(SO_4)_4(OH)_{12}$. The Pb-jarosite used in this study contained some 7 % K. Thus the formula should be written as $(K_{.07}Pb_{.93})Fe_6(SO_4)_4(OH)_{12}$. The molar mass is 1130.2. Hence the theoretical mass loss of water is 9.55 % and for SO_3 is 21.23 %. The TG and DTG curves for Pb-jarosite are shown in Figure 4. Two mass loss steps associated with dehydroxylation are observed at 390 and 418 °C. The experimentally determined mass loss is 11.2 % for both dehydroxylation steps. The mechanism for dehydroxylation is shown in steps 1 and 2 below. The third mass loss step of 13.7 % is observed at 531 °C and is attributed to the loss of SO_3 . This value is less than the theoretical value of 21.23 %. The chemical reaction associated with this mass loss step is shown in Step 3. Two higher temperature mass loss steps are observed at 759 and 812 °C and are assigned to the decomposition of $PbSO_4$.

Mechanism for decomposition

Step 1 Temperature 390 °C



Step 2 Temperature 418 °C



Step 3 Temperature 531 °C



Step 4 Temperature 759 °C



An early study using TGA methods showed that the plumbojarosite decomposed at 500 °C [5]. Another study suggested that the jarosite was completely dehydrated by 450 °C [25]. It was found that at temperatures above 550 °C further decomposition occurred with the loss of water and sulphur trioxide [25]. The thermal decomposition was complete by 950 °C. The final products were a mixture of hematite and PbO [25].

Conclusions

Thermogravimetric analysis coupled to a mass spectrometer has been used to study K, Na and Pb jarosites of Australian origin. K-jarosite shows a wide temperature range from 130 to 330 °C for water loss and a succession of mass losses at 501, 556, 598 and 622 °C. Mass loss steps for Na-jarosite are observed at (a) 215 and 230 °C (b) 316 and 352 °C and (c) 555, 575 and 595 °C. There is a four percent mass loss due to water loss at 215 and 230 °C. This water may be described as “excess water” resulting from the deprotonation of the Na-jarosite. For Pb-jarosite two mass loss steps associated with dehydroxylation are observed at 390 and 418 °C and a third mass loss step at 531 °C is attributed to the loss of SO₃. Two higher temperature mass loss steps are observed at 759 and 812 °C and are assigned to the decomposition of PbSO₄.

The Pb-jarosite contains some 7 % K. One possibility is that the K-jarosite was formed first and the Pb replaced the K with time. Jarosites are minerals which can function as collectors of heavy metals and low concentrations of heavy metals can be found in the natural jarosites. Such minerals can act as a significant heavy metal environmental sink [26]. Jarosites may be useful for the uptake of Ce⁶⁺ and As⁵⁺ in ground waters [27]. Such applications remain to be explored.

Acknowledgments

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Figure 4 Thermogravimetric and differential thermogravimetric analysis of Pb-jarosite

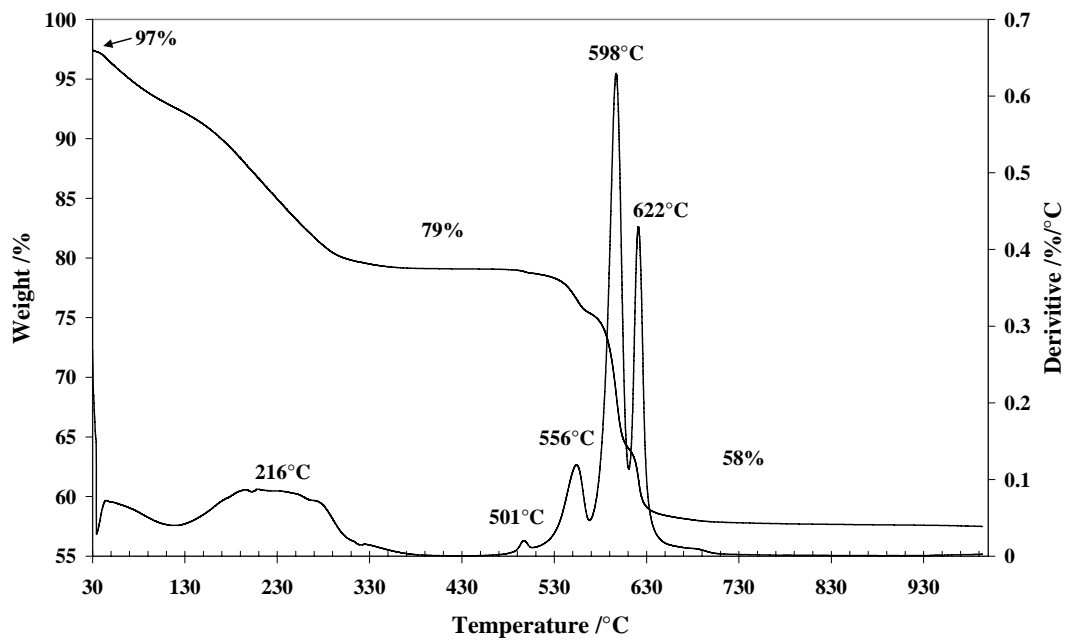


Figure 1

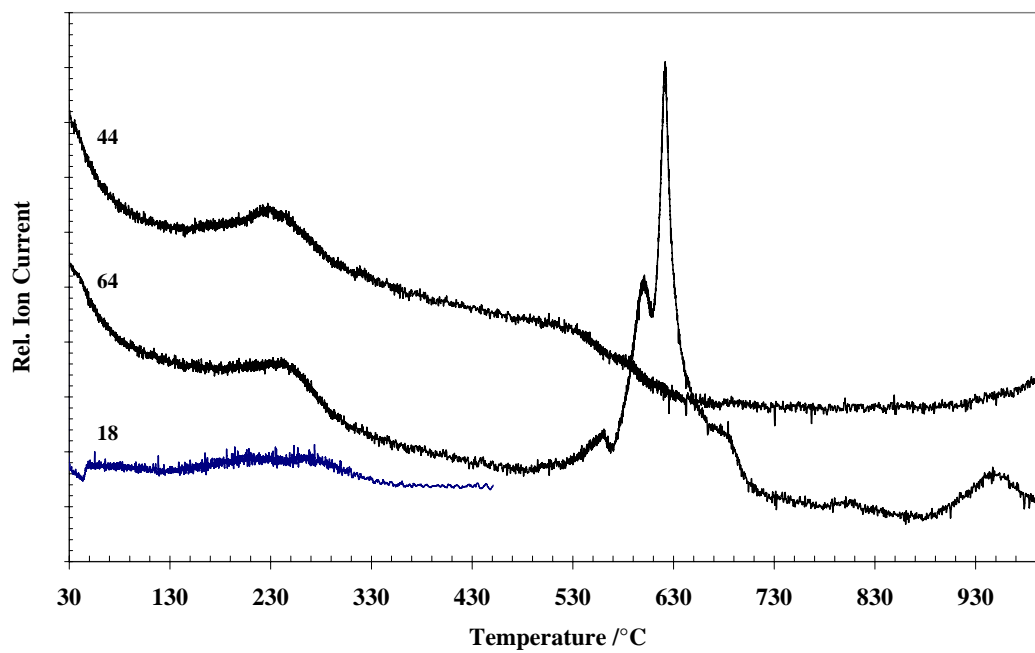


Figure 2

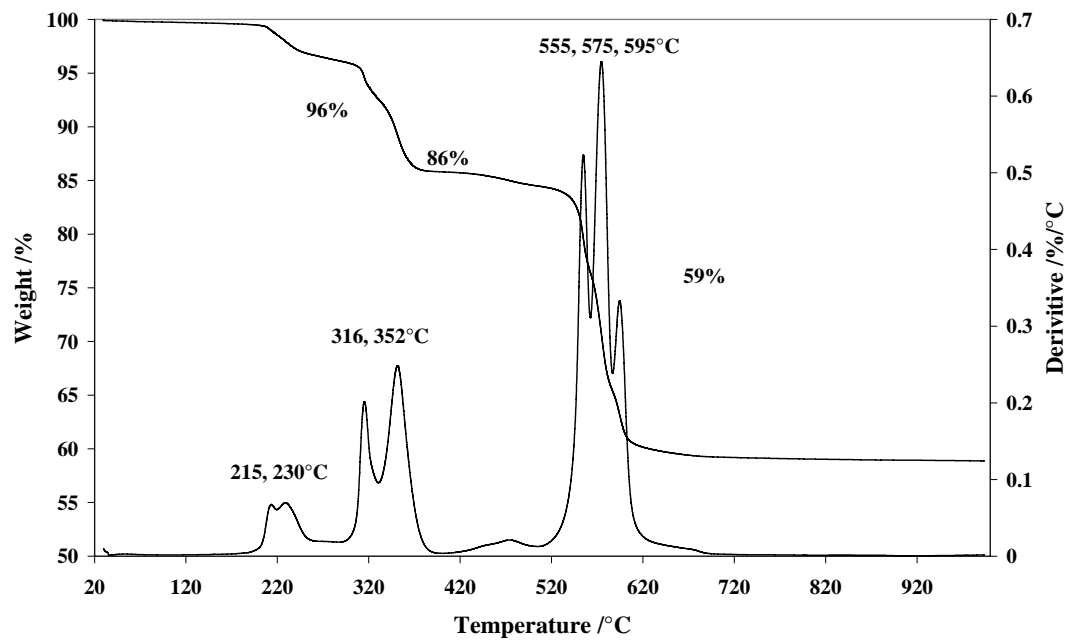


Figure 3

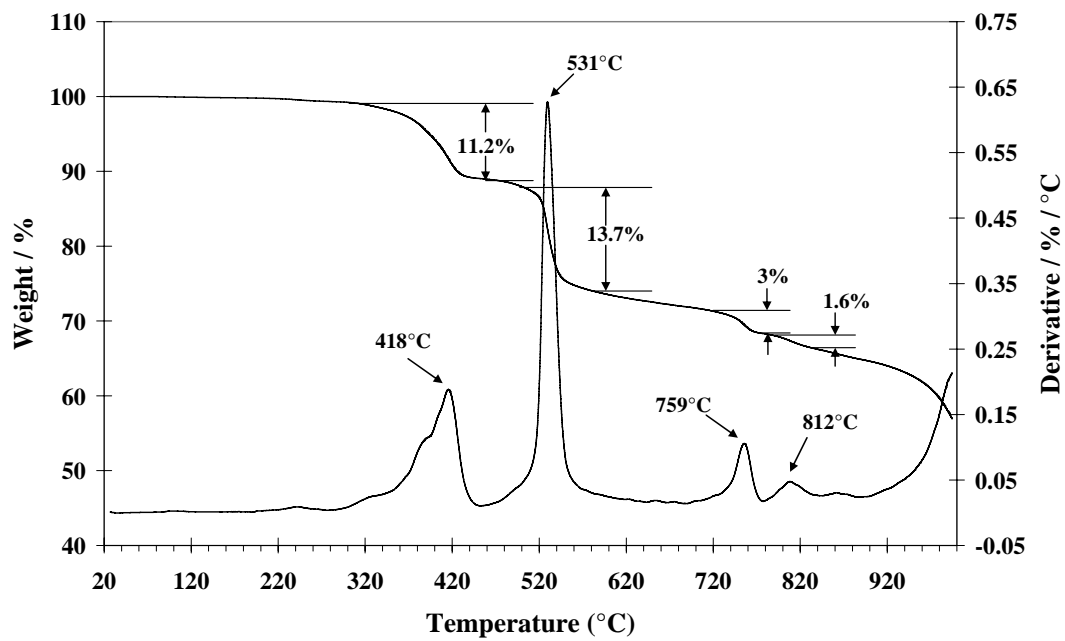


Figure 4