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Thermal decomposition of natural and synthetic plumbojarosites: Importance in ‘archeochemistry’

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Abstract

Plumbojarosite and argentoplumbojarosite were sources of lead and silver in ancient and medieval times. The understanding of the chemistry of the thermal decomposition of these minerals is of vital importance in ‘archeochemistry’. The thermal decomposition of plumbojarosite was studied using a combination of thermogravimetric analysis coupled to a mass spectrometer. Three mass loss steps are observed at 376, 420 and 502 °C. These are 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 jarosite were found to be less than that for the synthetic jarosite. This is attributed to a depression of freezing point effect induced by impurities in the natural jarosite. Raman spectroscopy was used to study the structure of plumbojarosite. Plumbojarosites are characterised by stretching bands at 1176, 1108, 1019 and 1003 $\mathrm{cm^{-1}}$ and bending modes at 623 and 582 $\mathrm{cm^{-1}}$. Changes in the molecular structure during thermal decomposition were followed by infrared emission spectroscopy. The technique shows the loss of intensity in the hydroxyl stretching region attributed to dehydroxylation. Loss of sulphate only occurs after dehydroxylation. Lead is formed at higher temperatures through oxygen evolution.
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Keywords: Jarosite; Plumbojarosite; Dehydration; Dehydroxylation; Infrared emission spectroscopy; Thermogravimetric analysis; Raman spectroscopy

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1. Introduction

The jarosite mineral group has been extensively studied [1]. Jarosite was first discovered in 1852 in ravines in the mountainous coast of southeastern Spain. Jarosite on Mars was discovered in 2004. 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)

Lead jarosite also known as plumbojarosite ($\mathrm{PbFe_6(SO_4)_4(OH)_{12}}$) was identified in relation to jarosite in 1902 [2]. Plumbojarosite is often found in cationic mixed jarosites [3–6]. Such minerals are of importance in medieval and archaeological science [7,8] and are also found in mine drainage sites both ancient and modern [6,8,9]. Such formation of jarosites has been occurring since the bronze age [10]. The importance of jarosite formation and its decomposition depends upon its presence in soils, sediments and evaporate deposits [11]. These types of deposits have formed in acid soils where the pH is less than 3.0 pH units [12]. Such acidification results from the oxidation of pyrite which may be from bacterial action or through air-oxidation.

The thermal decomposition of jarosites has been studied for some time [13–17]. Some studies of Pb-jarosite has been undertaken [14]. It was shown that decomposition occurred at 500 and 700 °C [14]. A later study showed that Pb-jarosite dehydrated at 450 °C and lost $\mathrm{SO_2}$ at temperatures >550 °C with total decomposition at 950 °C [6]. A later study reported the kinetics of decomposition of Pb-jarosite with decomposition occurring in three stages at 490, 750 and 950 °C [18].

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It has been stated that the thermal decomposition of jarosite begins at 400 °C with the loss of water [1]. 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 particular jarosite be it K, Na or Pb, etc., but normally goethite and hematite are formed together with soluble sulphates [19]. 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 [20–25]. In this work we report the thermal decomposition of natural and synthetic plumbojarosites.

2. Experimental

2.1. Minerals

To synthesise lead jarosite a 50 mL chloride solution was prepared. This solution contained 0.5 g $PbCl_2$, 12 mL of a saturated LiCl solution and 5 mL of 1.23 M $FeCl_3$ solution. (the high chloride concentration was necessary to prevent the precipitation of lead sulfate). 4.93 g $Fe_2(SO_4)_3$ was dissolved in the minimal volume of water and slowly added dropwise to the chloride solution. The final solution was heated for 21 h at 120 °C in an autoclave. A golden brown precipitate was collected under vacuum and then dried at 100 °C for an hour. 1.25 g of pure lead jarosite was obtained.

The natural Pb-jarosite originated 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 natural plumbojarosite contained 5% potassium. No other cations were found.

2.2. Thermal analysis

Thermal decomposition of the plumbojarosites was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). 34.4 mg of sample underwent thermal analysis, with a heating rate of 5 °C/min, resolution of 6–1000 °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, sulphur dioxide, sulphur trioxide, carbon dioxide and oxygen were analysed.

2.3. X-ray diffraction

X-ray diffraction patterns were collected using a Philips X'pert wide angle X-ray diffractometer, operating in step scan mode, with Cu Kα radiation (1.54052 Å). Patterns were collected in the range 3–90 ° 2*s* with a step size of 0.02° and a rate of 30 s per step. Samples were prepared as a finely pressed powder into aluminium sample holders. The Profile Fitting option of the software uses a model that employs twelve intrinsic parameters to describe the profile, the instrumental aberration and wavelength dependent contributions to the profile.

2.4. Infrared emission spectroscopy

FT-IR emission spectroscopy was carried out on a Nicolet spectrophotometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere. Approximately 0.2 mg of the plumbojarosite mineral was spread as a thin layer (approximately 0.2 microns) on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating.

In the normal course of events, three sets of spectra are obtained: first the black body radiation over the temperature range selected at the various temperatures, secondly the platinum plate radiation at the same temperatures and thirdly spectra from the platinum plate coated with the sample. Normally only one set of black body and platinum radiation data is required. The emittance spectrum (*E*) at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate from that of the platinum + sample, and the result rationed to the single beam spectrum of an approximate blackbody (graphite). The following equation was used to calculate the emission spectra.

$$E = -0.5 \times \log \frac{\mathrm{Pt} - S}{\mathrm{Pt} - C} \qquad (1)$$

This manipulation is carried out after all the data is collected. Emission spectra were collected at intervals of 50 °C over the range 200–750 °C. The time between scans (while the temperature was raised to the next hold point) was approximately 100 s. It was considered that this was sufficient time for the heating block and the powdered sample to reach thermal equilibrium. Spectra were acquired by 1064 scans over the temperature range 100–300 °C and 128 scans over the range 350–900 °C (approximate scan time 45 s), with a nominal resolution of 4 cm^{-1}.

Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used then spectra become difficult to interpret because of the presence of combination and overtone bands. Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction pattern for the synthetic plumbojarosite and the reference pattern (39-1353) for the natural plumbojarosite are shown in Fig. 1. Clearly the synthetic plumbojarosite corresponds well with the natural sample with no impurities that can be detected using the XRD technique.

3.2. Thermogravimetric analysis and mass spectrometric analysis

The TG and DTG curves for a synthetic and natural jarosite are shown in Fig. 2a and b, respectively. The ion current curves for the evolved gases water vapour and SO_3 from the synthetic plumbojarosite are shown in Fig. 3a and b. In terms of DTG patterns, there is a striking similarity between that of the synthetic and natural plumbojarosites. There is an apparent lowering of the temperatures of decomposition for the natural 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.

The ion current curves for evolved water vapour show water is evolved over a broad temperature range from 350 to 450 °C. Thus the 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 6 hydroxyl units as 3 H_2O. The experimentally determined mass losses for the synthetic and natural plumbojarosites are 11.8 and 11.2 %.

The ion current curve for evolved SO_3 (Fig 3b) shows that the mass loss for the synthetic plumbojarosite at 599 °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

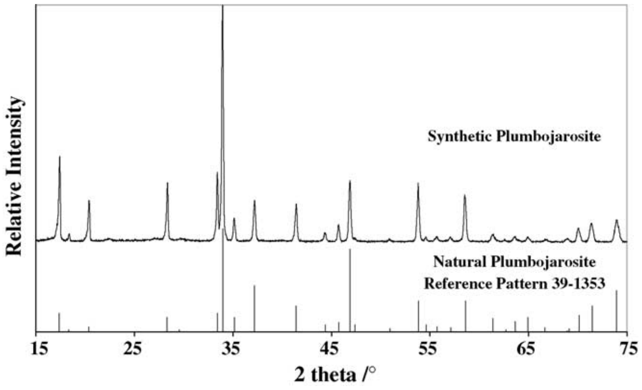

Fig. 1. XRD pattern for synthetic plumbojarosite and the reference pattern.

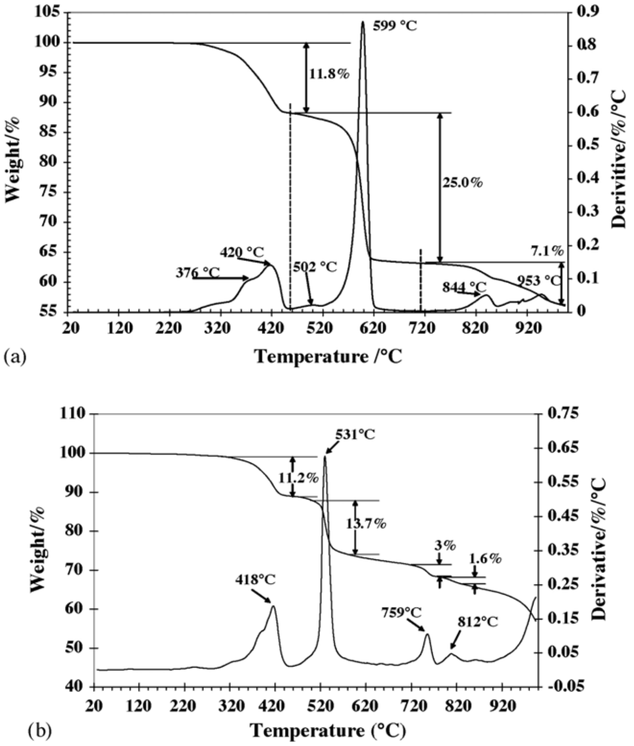

Fig. 2. (a) TG and DTG curves for synthetic plumbojarosite; (b) TG and DTG curves for natural plumbojarosite.

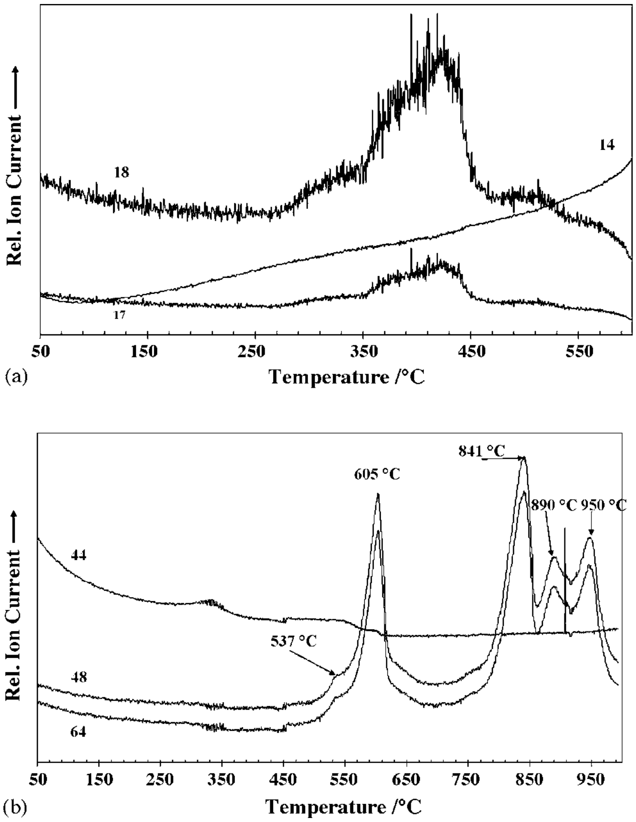

Fig. 3. (a) Ion current for masses 17 and 18 and (b) ion current for masses 44, 48 and 64.

presence of impurities in the natural sample. The experimental mass loss is 25%. If all four 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 the synthetic 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.

3.3. 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 and (c) loss of oxygen.

- Stage 1
- $PbFe_6(SO_4)_4(OH)_{12} \rightarrow PbFe_6(SO_4)_4O_6 + 6H_2O$
- Theoretical mass loss of 9.56%.
- Experimental mass loss 11.8%.
- Temperature of mass loss 376 and 420 °C.

- Stage 2
- $Pb(FeO)_6(SO_4)_4 \rightarrow PbO_{3.5}(FeO)_6(SO_4)_{0.5} + 3.5SO_3$
- Theoretical mass loss of 24.77%.
- Experimental mass loss for the synthesised plumbojarosite is 25%.
- Temperature of mass loss is 599 °C.

- Stage 3
- $PbO_{3.5}(FeO)_6(SO_4)_{0.5} \rightarrow Pb + 3Fe_2O_3 + 0.5O_2 + 0.5SO_3$
- Theoretical mass loss of 4.96%.
- Experimental mass loss for the synthesised plumbojarosite is 5.6%.
- Temperature of mass loss is 844 and 953 °C.

3.4. Raman and infrared spectroscopy

One technique for studying the changes in the molecular structure during thermal decomposition is infrared emission spectroscopy. The technique enables the spectrum at the elevated temperature to be determined. In order to understand the spectrum at the elevated temperature it is necessary to understand the room temperature spectra. A comparison of the Raman spectra of the natural and synthetic plumbojarosite are shown in Fig. 4. The Raman and infrared spectra of the lead jarosite are shown in Fig. 5. Sulphates as with other oxyanions lend themselves to analysis by Raman spectroscopy. In aqueous systems, the sulphate anion is of T_d symmetry and is characterised by Raman bands at 981 cm^{-1} (ν_1), 451 cm^{-1} (ν_2), 1104 cm^{-1} (ν_3) and 613 cm^{-1} (ν_4). Reduction in symmetry in the crystal structure of sulphates such as jarosites will cause the splitting of these vibrational modes. For jarosites the space group is C_5^3 and six sulphate fundamentals should be observed. The Raman band at 1036 cm^{-1} is attributed to the SO_4^{2-} symmetric stretching mode. The equivalent infrared band is forbidden and is not observed.

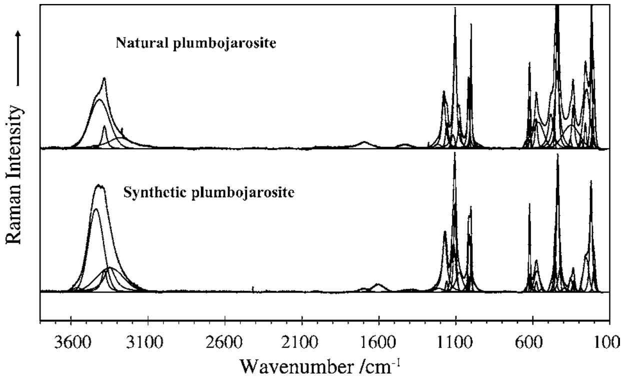

Fig. 4. Comparison of the Raman spectra of natural and synthetic plumbojarosite.

A previous study by Sasaki reported the two Pb-jarosite symmetric stretching band at 1015 and 1002 cm^{-1} which is in excellent agreement with the value reported in this research [26]. The two Raman bands at 1099 and 1062 cm^{-1} are assigned to the SO_4^{2-} antisymmetric stretching modes. The two equivalent infrared bands are the two bands at 1182 and 1109 cm^{-1}. Sasaki reported the Raman bands for Pb-jarosite as 1107 and 1161 cm^{-1} in the Raman spectrum and 1080, 1092 and 1195 cm^{-1} in the infrared spectrum [26]. The band

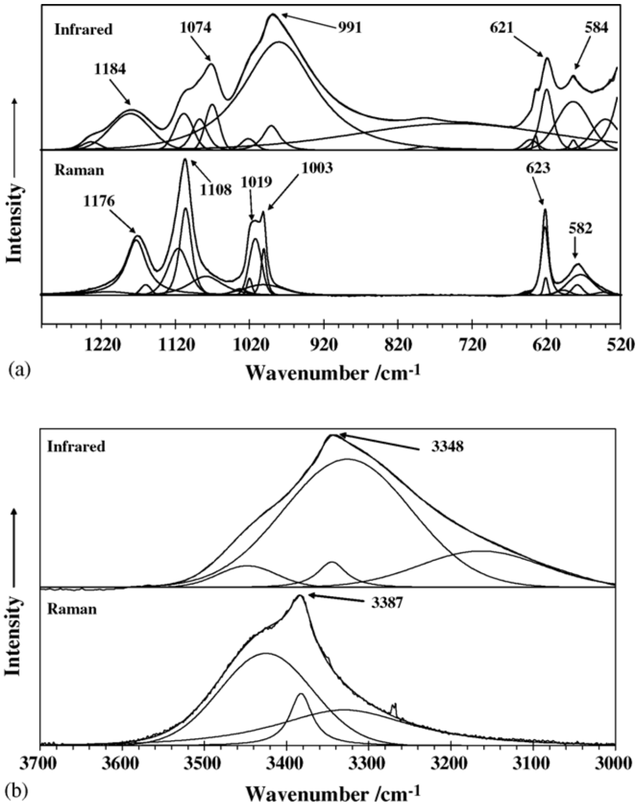

Fig. 5. (a) Raman and infrared spectra and their component bands of synthetic plumbojarosite in the 520–1220 cm^{-1} region and (b) Raman and infrared spectra and their component bands of synthetic plumbojarosite in the hydroxyl stretching region.

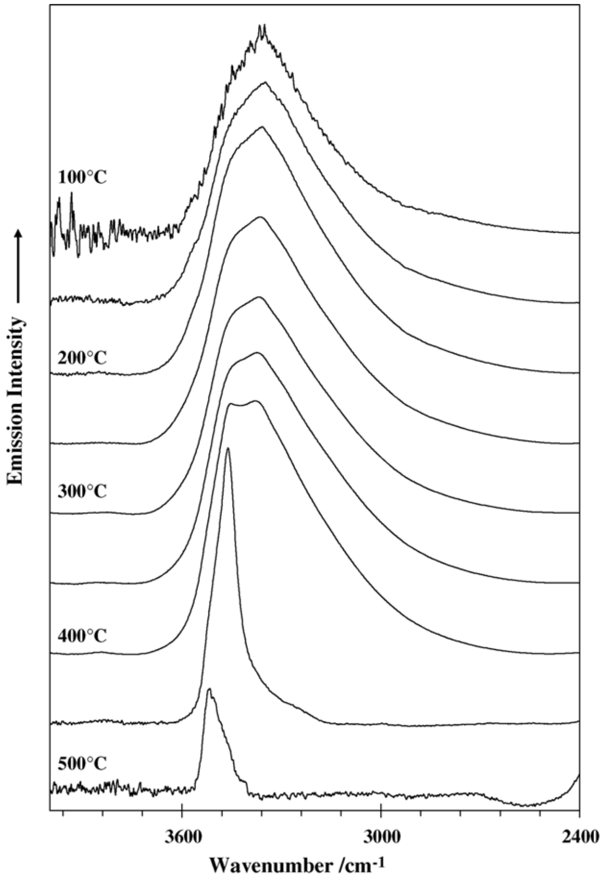

Fig. 6. IES of plumbojarosite in the hydroxyl stretching region.

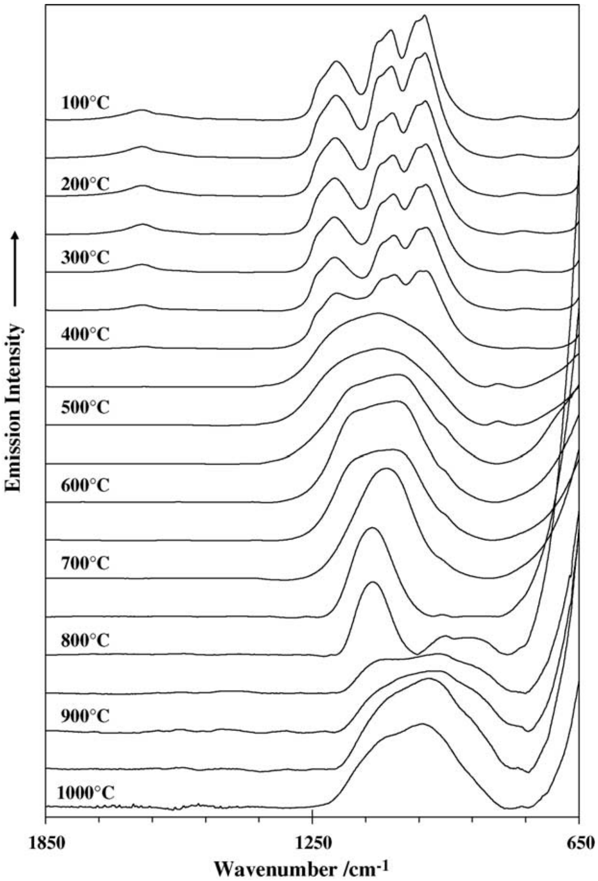

Fig. 7. IES of plumbojarosite in the 550–1850 cm^{-1} region.

at 619 cm^{-1} in the infrared spectrum and at 674 cm^{-1} in the Raman spectrum is ascribed to the ν_4 bending mode of the SO_4^{2-}units. The previous study, which reported the Raman spectrum of Pb-jarosite gave two bands at 623 and 668 cm^{-1} in the infrared spectrum and at 623 cm^{-1} in the Raman spectrum [26]. In the Raman spectrum bands at 424 and 454 cm^{-1} are attributed to the ν_2 bending modes of the $SO_4{}^{2-}$ units.

3.5. *Infrared emission spectroscopy*

Thermal decomposition of the lead jarosite may also be followed using infrared emission spectroscopy in which the infrared spectrum can be obtained in situ at the elevated temperature. The infrared emission spectra of synthetic plumbojarosite are shown in Figs. 6 and 7. The figure shows that the intensity of the OH stretching region decreases as the temperature is raised. No intensity remains after 500 °C. Three bands are observed in the infrared spectra at 100 °C at 3400.6, 3250.2 and 2992.9 cm^{-1}. In the 500 °C spectrum only a single band at 3503.3 cm^{-1} is found. The IES data shows that dehydroxylation is complete by 500 °C. Such a result is in harmony with the results of the DTG. DTG showed three mass loss steps 376, 420 and 502 °C.

The IES data show that the spectra of the sulphate stretching region remains unchanged over the 100–400 °C. Four bands are identified at 1194.8, 1106.4, 1073.4 and 1023.0 cm^{-1}. These bands are attributed to the sulphate antisymmetric stretching modes. In the 450 °C spectrum, a single broad band is found at 1092 cm^{-1}. No changes are observed in the spectra until after dehydroxylation has taken place.

4. Conclusions

Understanding the chemistry of plumbojarosite and argentoplumbojarosite is of importance in archeochemistry. Plumbojarosite was a source of lead in pre- and Roman times. Argentoplumbojarosite 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 argentoplumbojarosite. 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.

The thermal decomposition of a natural and synthetic plumbojarosite has been studied using thermogravimetric analysis and mass spectrometry. The temperatures of the thermal decomposition of the natural jarosite were found to be less than that for the synthetic jarosite. 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.

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