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Thermal decomposition of synthetic argentojarosite—Implications for silver production in medieval times

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Abstract

The thermal decomposition of argentojarosite has been studied by thermogravimetric, spectroscopic and infrared emission techniques. Dehydroxylation 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. Changes in the structure of argentojarosite are also followed by the infrared emission spectra. The intensity of hydroxyl stretching vibration approaches zero by 400 °C confirming the loss of hydroxyl units by this temperature. At this temperature changes in the infrared spectra of the sulphate units occurs. The intensity of the sulphate stretching vibrations approaches zero by 750 °C. 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.

Keywords: Argentojarosite; Jarosite; Plumbojarosite; Dehydration; Dehydroxylation; Raman spectroscopy; Infrared emission spectroscopy; Thermogravimetric analysis

1. Introduction

Argentojarosite ($AgFe_3^{3+}(SO_4)_2(OH)_6$)was first identified in 1923 from the Titanic Standard mine at Dividend, Utah, USA [1]. It has since been identified in at least 14 other US sites. The mineral in some localities is of sufficient abundance as to be a silver bearing ore [2]. Argentojarosite was exploited at Rio Tinto, Spain, from Roman or even pre-Roman times [3]. Argentojarosites had an important influence on the wealth of both Europe and South America [4].

The thermal decomposition of jarosites has been studied for some considerable time [5–9]. However, no thermal studies on the pure end member of argentojarosite have been forthcoming, nor has there been studies on argentoplumbojarosites [6]. It has been stated that the thermal decomposition of jarosite begins at 400 °C with the loss of water [10]. The process is apparently kinetically driven. Water loss can occur at low temperatures over extended periods of time [10]. 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 [11].

2. Experimental

2.1. Synthesis of the argentojarosite

Argentojarosite was synthesised by dissolving 4.8 g $Fe_2(SO_4)_3$ in 120 mL of water. 0.108 g of $AgNO_3$ was added to the solution followed by a further 30 mL of water. The solution was heated in a covered Erhlenmeyer flask for 22 h at 95 °C. The resulting yellow–brown precipitate was collected and dried under vacuum. Powder X-ray diffraction proved the correct structure was obtained.

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2.2. Thermal analysis

Thermal decomposition of the argentojarosite was carried out in a TA® Instruments (series Q500) in a nitrogen atmosphere (80 cm^3/min). 34.4 mg of sample with a heating rate of 5 °C/min, resolution of 6 to 1000 °C. Several replicates were analysed. The products of the thermal decomposition were analysed by PXRD. The furnace temperature was regulated 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 for the determination of water vapour, sulphur dioxide, sulphur trioxide, carbon dioxide and oxygen.

2.3. Raman spectroscopy

The crystals of the argentojarosite were oriented on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objectives and part of a Renishaw 1000 Raman microscope system. Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated with the 520.5 cm^{-1} line of a silicon wafer. To ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique [12–18].

2.4. Infrared spectroscopy

Infrared spectra were obtained with a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

FTIR 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 [19–25]. Approximately, 0.2 mg of the aregentojarosite mineral was spread as a thin layer (approximately 0.2 μm) on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. 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 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}. Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation was performed with the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

3. Results and discussion

3.1. Thermogravimetric analysis and mass spectrometric analysis

The TG analysis of the synthetic argentojarosite together with the DTG analysis is shown in Fig. 1. The ion current

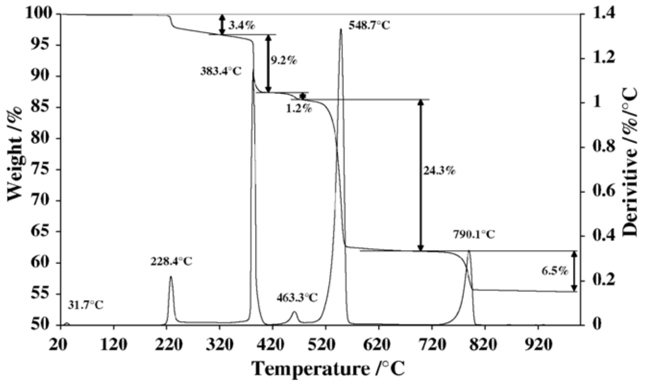

Fig. 1. Thermogravimetric and differential thermogravimetric analysis of argentojarosite.

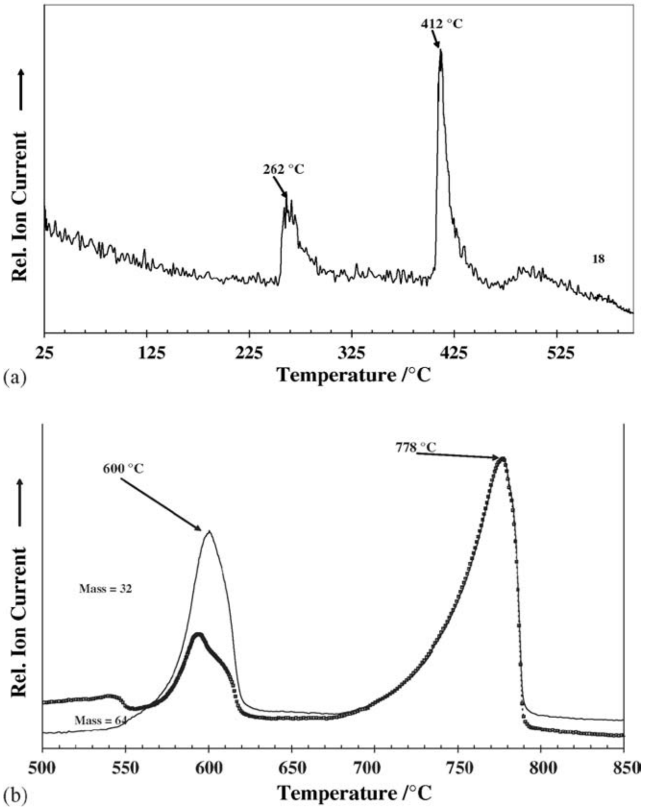

Fig. 2. Ion current curves (a) for evolved water vapour as a function of temperature and (b) for oxygen and sulphur dioxide as a function of temperature.

curves for mass 18 are shown in Fig. 2a. The ion current curves for masses 32 and 64 are shown in Fig. 2b. The small mass loss at 31.7 °C is ascribed to the loss of physically adsorbed water. Differences in the temperatures of the mass loss, TG and the ion current of the evolved gases resulted from the TG and mass spectrometry analyses being undertaken on different samples. Nevertheless, the ion current of the evolved water vapour clearly shows the mass loss step at 228 °C is due to dehydroxylation. The mass loss is 3.4%, which corresponds to the loss of one water molecule, theoretical mass loss 3.16%. The second mass loss at 383.4 °C corresponds to a mass loss of 2.5 moles of water due to dehydroxylation. The mass loss of 1.58% at 463 °C does not correspond to the loss of sulphate as sulphur dioxide or sulphur trioxide. The ion current curve of evolved water vapour does show a broad feature at 490 °C, which appears to correspond with the 463 °C mass loss. The reason for the different temperatures was that the TG and evolved ion current analyses were conducted at different rates. The ion current experiment was conducted at a considerable faster rate than the thermal analysis.

The biggest mass loss occurs at 548.7 °C with a mass loss of 24.3%. The ion current curves show this mass loss is due entirely to the loss of sulphur dioxide, compares favourably with the theoretical mass loss of 25.38%. The mass loss at 790 °C corresponds to loss of oxygen. The ion current curve shows a temperature of 778 °C. The products of the thermal decomposition of argentojarosite as determined by XRD analysis are hematite and silver metal.

3.2. Infrared emission spectroscopy

The use of infrared emission spectroscopy enables the changes in the structure of the argentojarosite to be followed in situ at elevated temperatures. As the material is heated, the infrared radiation is emitted and is detected by the infrared detector. The infrared emission spectra of Ag-jarosite in the OH stretching region are shown in Fig. 3 over the 100–400 °C temperature range. No intensity remains in this band above 400 °C. showing dehydroxylation of the Ag-jarosite is complete by this temperature. The IE spectra of the sulphate stretching region are shown in Fig. 4. In the IE spectrum at 100 °C, four bands are observed at 1205, 1091, 1024 (shoulder) and 1010 cm^{-1}. The bands show a slight red shift with temperature increase. No changes are observed in the spectral profile until after 350 °C at which point dehydroxylation has taken place. The definition and resolution of the bands is lost at 550 °C and no intensity remains in the spectra at 750 °C;

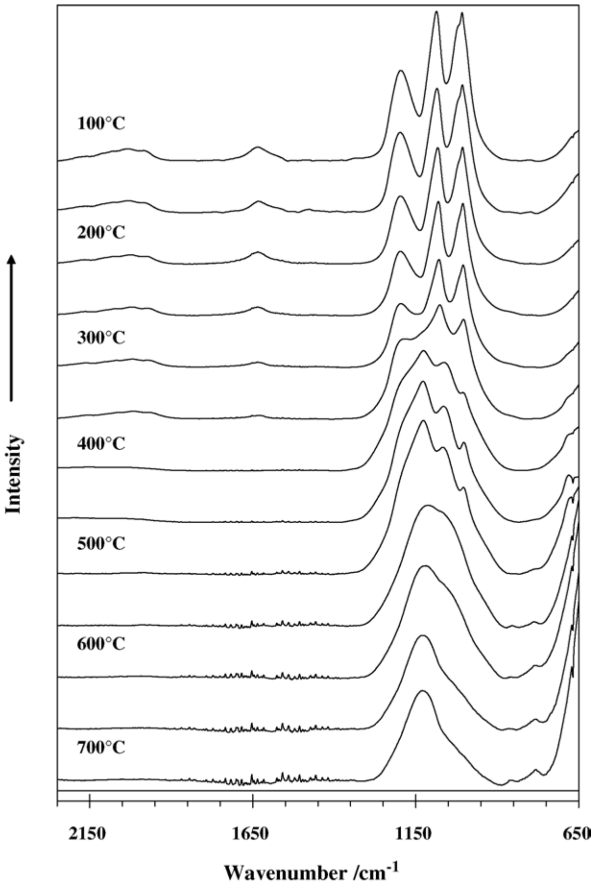

Fig. 3. Infrared emission spectra of the hydroxyl-stretching region of argentojarosite.

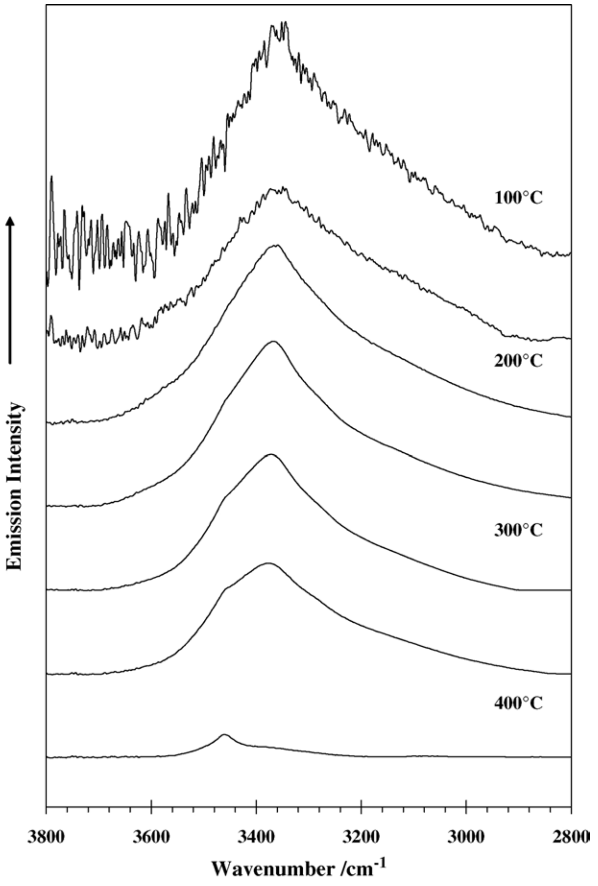

Fig. 4. Infrared emission spectra of the 650–2250 cm^{-1} region of argentojarosite.

thus showing that the loss of sulphate has occurred by this temperature.

4. Conclusions

Argentojarosite was exploited at Rio Tinto, Spain from Roman and even pre-Roman times for silver production [26]. Argentojarosites had an important influence on the accumulation of wealth of both Europe and South America [26]. Thermal analysis shows the relatively low temperatures at which argentojarosite can be converted to metallic silver. The existence of large quantities of argentojarosite and argentoplumbojarosite resulted in the formation of large quantities of metallic silver.

Acknowledgments

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References

[1] W.T. Schaller, J. Wash. Acad. Sci. 13 (1923) 233.
[2] C.A. Schempp, Am. J. Sci. 6 (1923) 73.
[3] J.E. Dutrizac, J.L. Jambor, J.B. O'reilly, CIM Bull. 76 (1983) 78.
[4] J.E. Dutrizac, J.L. Jambor, Rev. Miner. Geochem. 40 (2000) 405.
[5] S. Nagai, N. Yamanouchi, Nippon Kagaku Kaishi 52 (1949) 83.
[6] J.L. Kulp, H.H. Adler, Am. J. Sci. 248 (1950) 475.
[7] G. Cocco, Periodico di Mineralogia 21 (1952) 103.
[8] A.I. Tsvetkov, E.P. Val'yashikhina, Doklady Akademii Nauk SSSR 89 (1953) 1079.
[9] A.I. Tsvetkov, E.P. Val'yashikhina, Doklady Akademii Nauk SSSR 93 (1953) 343.
[10] J.E. Dutrizac, J.L. Jambor, Chapter 8 Jarosites and Their Application in Hydrometallurgy, 2000, 405.
[11] P.S. Thomas, D. Hirschausen, R.E. White, J.P. Guerbois, A.S. Ray, J. Therm. Anal. Calorim. 72 (2003) 769.
[12] R.L. Frost, J. Raman Spectrosc. 35 (2004) 153.
[13] R.L. Frost, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. A 60 (2004) 1439.
[14] R.L. Frost, O. Carmody, K.L. Erickson, M.L. Weier, D.O. Henry, J. Cejka, J. Mol. Struct. 733 (2004) 203.
[15] R.L. Frost, L. Duong, M. Weier, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 60 (2004) 1853.
[16] R.L. Frost, M. Weier, Neues Jahrbuch fuer Mineralogie, Monatshefte (2004) 445.
[17] R.L. Frost, M.L. Weier, J. Raman Spectrosc. 35 (2004) 299.
[18] R.L. Frost, M.L. Weier, M.O. Adebajo, Thermochim. Acta 419 (2004) 119.
[19] R.L. Frost, A.M. Vassallo, Clays Clay Miner. 44 (1996) 635.
[20] R.L. Frost, G.A. Cash, J.T. Kloprogge, Vib. Spectrosc. 16 (1998) 173.
[21] R.L. Frost, J.T. Kloprogge, Tijdschr Klei Glas Keram. 19 (1998) 11.
[22] R.L. Frost, H. Ruan, J.T. Kloprogge, Internet J. Vib. Spectrosc. 4 (2000) 1.
[23] R.L. Frost, K.L. Erickson, Thermochim. Acta 421 (2004) 51.
[24] R.L. Frost, N.K. Roberts, Springer Series Surf. Sci. 23 (2003) 203.
[25] R.L. Frost, Z. Ding, H.D. Ruan, J. Therm. Anal. Calorim. 71 (2003) 783.
[26] J.E. Dutrizac, J.L. Jambor, Appl. Miner., Proc. Int. Congr. Appl. Miner. Miner. Ind. 2 (1985) 507.