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A thermogravimetric study of the alunites of sodium, potassium and ammonium

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Abstract

Thermogravimetry in tandem with mass spectrometry has been used to characterise the thermal decomposition of synthetic alunites of potassium, sodium and ammonium. Three mechanisms of decomposition are observed (a) dehydration, (b) dehydroxylation and (c) desulphation. The thermal decomposition of the three alunites is different. For NH_4-alunite, an additional process of de-ammoniation is observed which occurs simultaneously with dehydration. Dehydroxylation takes place in a series of four steps. De-sulphation occurs for K-alunite at 680 °C in a single step in comparison with Na and NH_4 alunites where de-sulphation is observed in a series of four steps. The temperature of desulphation is cation dependent. The thermal decomposition is not completed until around 800 °C.

Keywords: Alunite; Natroalunite; Ammonioalunite; Jarosite; Thermogravimetry; Sulphate

1. Introduction

Interest in the chemistry of alunites stems from a number of reasons. Firstly there is the possible discovery of alunites on Mars [1,2]. Such a find implies the presence of water either at present or at some time in the planetary past [3,4]. Interest in such minerals and their thermal stability rests with the possible identification of these minerals and dehydrated paragenetically related minerals on planets [5]. There have been many studies on related minerals such as the Fe(II) and Fe(III) sulphate minerals [6–11]. The importance of alunite formation and its decomposition depends upon its presence in soils, sediments and evaporite deposits [12]. These types of deposits have formed in acid soils where the pH is less than 3.0 pH units [13]. Such acidification results from the oxidation of pyrite which may be from bacterial action or through air-oxidation. Thirdly alunites are important from an environmental point of view. Alunites are minerals which can function as collectors of heavy metals and low concentrations can be found in the natural alunites. Such minerals can act as a significant environmental sink [14]. One of the difficulties associated with the analysis of alunites is that they are often poorly crystalline, making detection using XRD techniques difficult. Another problem associated with the study of alunites is their thermodynamic stability [15]. Often the minerals are formed from acid-sulfate rich environments such as acid mine drainage and acid-sulfate soils and as such their solubility is controlled by climatic conditions, in particular the temperature.

Alunites are a group of minerals which form part of the alunite supergroup [16]. The general formula is given by $DG_3(TO_4)_2(OH,H_2O)_6$ where the D sites are occupied by either monovalent cations such as K, Na, NH_4, H_3O^+ and others, or divalent cations such as Ca, Ba, Sr, Pb, or trivalent cations, for example, Bi. G is the trivalent cation either Al or Fe^{3+} and T is S^{6+}, As^{5+} or P^{5+}. Alunites can be divided into alunites and jarosites simply depending on whether the concentration of Al is >Fe (alunites) or Fe > Al (jarosites) [15]. Of course solid solution formation can exist across a wide range of concentrations and substitutions. Common members of the alunite group are alunite $KAl_3(SO_4)_2(OH)_6$, natroalunite $NaAl_3(SO_4)_2(OH)_6$, ammonioalunite $NH_4Al_3(SO_4)_2(OH)_6$, sclossmacherite $(H_3O^+,Ca^{2+})Al_3(SO_4)_2(OH)_6$. The structure of alunites is well known [17–19] and is trigonal with a 6.990, c 16.905 Å space group *R3m*, with $Z = 3$.

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Interestingly there have been few recent studies on the thermal analysis of alunites [20]. The reason for this is unclear. Perhaps it is because of the variation in composition which occurs with natural minerals. Such variation can be overcome with the use of synthetic minerals. The first recorded thermal analysis of alunite occurred in 1919 [21]. Early studies focussed on the effect of alunite impurity on the thermal treatment of other chemicals [22–26]. Many studies occurred when new equipment became available [27–40]. Recently, thermal analysis has been used to enhance the understanding of the stability of minerals which may be found on planets [5,41–51]. In this work, as part of our studies of secondary mineral formation and their stability, we report the comparison of the thermal analysis of selected synthetic alunites.

2. Experimental

2.1. Minerals

The alunites were synthesised according to the following recipes.

2.1.1. Synthesis procedure of ammonium alunite

5.16 g of $(NH_4)_2SO_4$ was dissolved in 40 ml of water. The solution was transferred to an autoclave and 3 g of crystalline $Al(OH)_3$ added over a 5 min period. The autoclave was then heated to 120 °C for 2 days. The crystalline white solid formed was collected under vacuum filtration and dried. Samples were dried in a vacuum desiccator at room temperature. 2.86 g of the product was collected and this was identified by X-ray diffraction as ammonium alunite.

2.1.2. Synthesis procedure of sodium alunite

0.82 g Na_2SO_4 and 5.9 g $Al_2(SO_4)_3$ were dissolved in 40 ml of water. This solution was covered and heated on a hotplate at 150 °C for 4 h. The small amount of white precipitate was collected under vacuum and dried for 4 days. The sample was identified as sodium alunite by X-ray diffraction.

2.1.3. Synthesis procedure of potassium alunite

One gram of K_2SO_4 and 5.9 g of $Al_2(SO_4)_3$ were dissolved in 40 ml of water. The solution was heated at 150 °C in an autoclave for 19 h. A white crystalline precipitate was collected and dried under vacuum. The sample mass was 0.93 g. The product was identified by X-ray diffraction as potassium alunite.

2.2. Thermal analysis

Thermal decompositions of alunites were carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere ($80\ cm^3/min$). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 2.0 °C/min up to 1000 °C. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. The following gases/units were analyzed: O_2, S, SO_3, SO_2, OH and H_2O. Mass/charge ratios are measured for example O_2 is 32/1 and 32/2.

Band component analysis of the DTG curves was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss–Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

2.3. X-ray diffraction

X-ray diffraction (XRD) patterns were recorded using Cu Kα radiation ($n = 1.5418$ Å) on a Philips PANalytical X' Pert PRO diffractometer operating at 45 kV and 35 mA with 0.125° divergence slit, 0.25° anti-scatter slit, between 3 and 65° (2θ) at a step size of 0.0167°.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of potassium, sodium and ammonium alunite are shown in Fig. 1a–c. The figures compare the XRD patterns with the published data. The XRD patterns show some background in the 20–30° two theta. This simply means that some of the synthesised product shows some amorphicity.

3.2. Thermogravimetric analysis

3.2.1. Potassium alunite

The thermogravimetric analysis of potassium alunite is shown in Fig. 2. The mass spectra of evolved gases are reported in Fig. 3. Three major processes occur for the thermal decomposition of K-alunite. These are dehydration, dehydroxylation and desulphation. The details of these processes are listed below.

3.3. Mechanism for decomposition of potassium alunite

Step 1 Dehydration
Temperature up to ∼220 °C

$$KAl_3(SO_4)_2(OH)_6{\cdot}xH_2O \rightarrow KAl_3(SO_4)_2(OH)_6 + xH_2O$$

This step represents the dehydration step and occurs over a long temperature range starting at ∼50 °C. The wide temperature range for dehydration shows that water is strongly adsorbed to the alunite surfaces.

Step 2 Dehydroxylation

Step 2a At 265 and 284 °C

$$KAl_3(SO_4)_2(OH)_6 \rightarrow KO_{1/2}Al_3(SO_4)_2(OH)_5 + (1/2)\cdot H_2O$$

This step represents the loss of one hydroxyl unit from the K-alunite structure.

The MW of alunite is 414 and the % mass of OH units is 24.6%. Thus, there is 4.1% mass loss per OH unit. The mass loss at 265 °C is 4.8% which represents the loss of one OH unit.

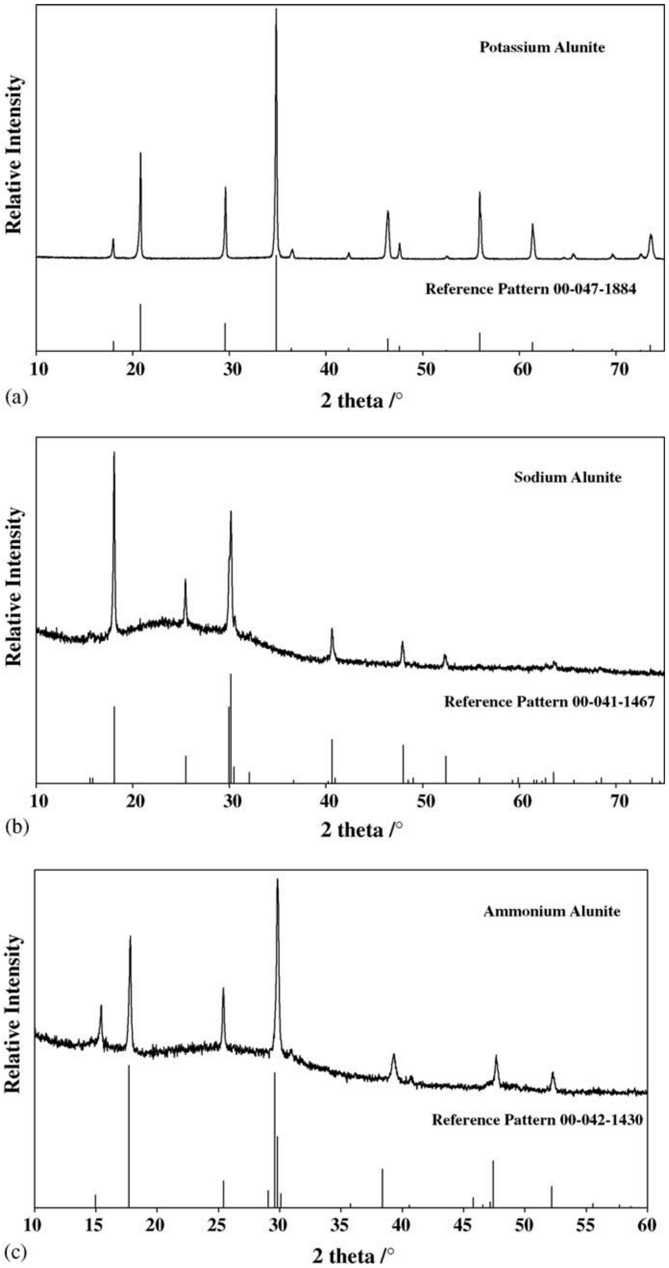

Fig. 1. (a) X-ray diffraction pattern of synthetic potassium alunite and the potassium alunite reference pattern (00-047-1884); (b) X-ray diffraction pattern of synthetic sodium alunite and the sodium alunite reference pattern (00-041-1467) and (c) X-ray diffraction pattern of synthetic ammonium alunite and the ammonium alunite reference pattern (00-042-1430).

The ion current curves for the evolved gases show for $m/z = 18$ and 16 a mass gain at 281 °C. The mass gain in the MS curves corresponds precisely with the mass loss in the TG curves.

Step 2b At 403 °C

$$KO_{1/2}Al_3(SO_4)_2(OH)_5 \rightarrow KOAl_3(SO_4)_2(OH)_4 + (1/2)\cdot H_2O$$

The mass loss at this step is 3.68% which may be equated to the loss of one OH unit. In the equation above the oxygen have been associated with the K. This is a matter of convenience. The ion current curves for the evolved gases show for $m/z = 18$ and 17 a mass gain at 406 °C. The mass gain in the MS curves corresponds with the mass loss in the TG curves.

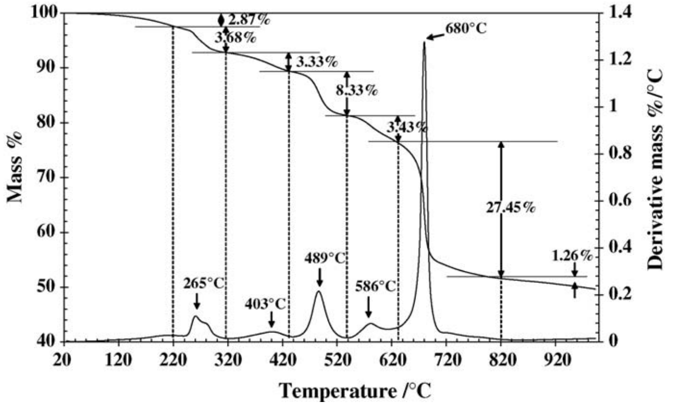

Fig. 2. Thermogravimetric analysis and differential thermogravimetric analysis of potassium alunite.

Step 2c At 489 °C

$$KOAl_3(SO_4)_2(OH)_4 \rightarrow KO_2Al_3(SO_4)_2(OH)_2 + H_2O$$

There is a mass loss of 8% which represents the mass of two OH units. The ion current curves for the evolved gases show for $m/z = 18$ and 17 a mass gain at 490 °C. The mass gain in the MS curves corresponds with the mass loss in the TG curves.

Step 2d At 586 °C

$$KO_2Al_3(SO_4)_2(OH)_2 \rightarrow KO_3Al_3(SO_4)_2 + H_2O$$

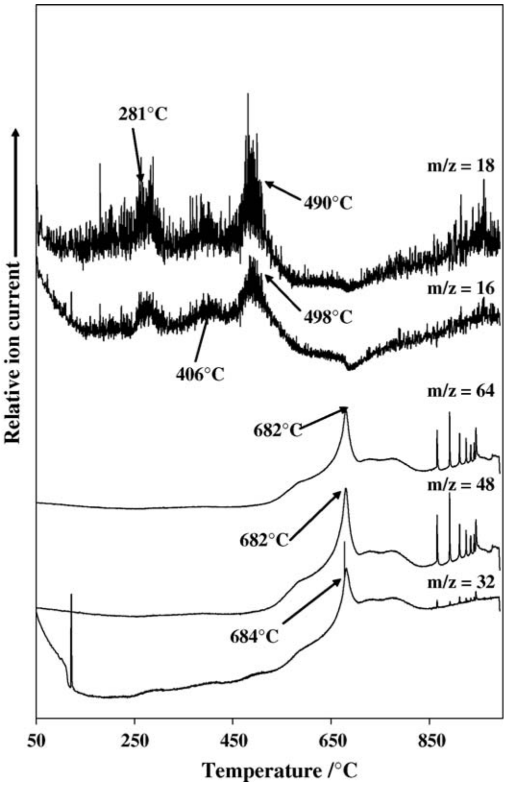

Fig. 3. Ion current curves for the evolved gases from the decomposition of potassium alunite.

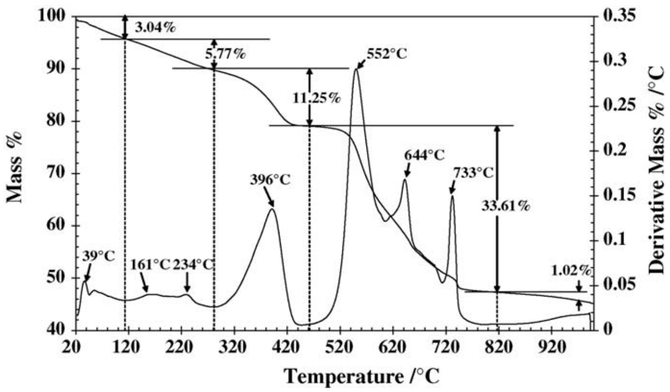

Fig. 4. Thermogravimetric analysis and differential thermogravimetric analysis of sodium alunite.

At this step there is a mass loss of 3.43% which must represent the loss of the final OH units. No distinct peak is observed in the ion current curves for $m/z = 18$, 17 and 16 at 586 °C. However, the peaks at 490 °C is broad and there is a higher temperature tail to this peak. It is proposed that the OH units for K-alunite come off in a series of four steps at ∼265, 403, 489 and 586 °C.

Step 3 Desulphation
Loss of sulphate
Temperature 680 °C

$$KO_3Al_3(SO_4)_2 \rightarrow 1/2K_2SO_4 + SO_3 + 1.5Al_2O_3 + 2.5O_2$$

The TG and DTG curves show a large mass loss of 24.6% at 680 °C. The ion current curves for $m/z = 64$, 48 and 32 all show a peak at 682 °C confirming the loss of sulphate at this temperature.

3.3.1. Sodium alunite

The thermogravimetric analysis of sodium alunite is shown in Fig. 4. The mass spectra of evolved gases are reported in Fig. 5. Just as for K-alunite three major processes occur for the thermal decomposition of K-alunite. These are dehydration, dehydroxylation and desulphation. The details of these processes are listed below.

3.4. Mechanism for decomposition of potassium alunite

Step 1 Dehydration
Temperature up to ∼120 °C

$$NaAl_3(SO_4)_2(OH)_6{\cdot}xH_2O \rightarrow NaAl_3(SO_4)_2(OH)_6 + xH_2O$$

This step represents the dehydration step and occurs over a long temperature range starting at room temperature. The wide temperature range for dehydration shows that water is strongly adsorbed to the Na-alunite surfaces.

Step 2 Dehydroxylation
Step 2a At 161 and 234 °C

$$NaAl_3(SO_4)_2(OH)_6 \rightarrow NaO_{0.5}Al_3(SO_4)_2(OH)_5 + 1/2H_2O$$

This step represents the loss of one hydroxyl unit from the Na-alunite structure.

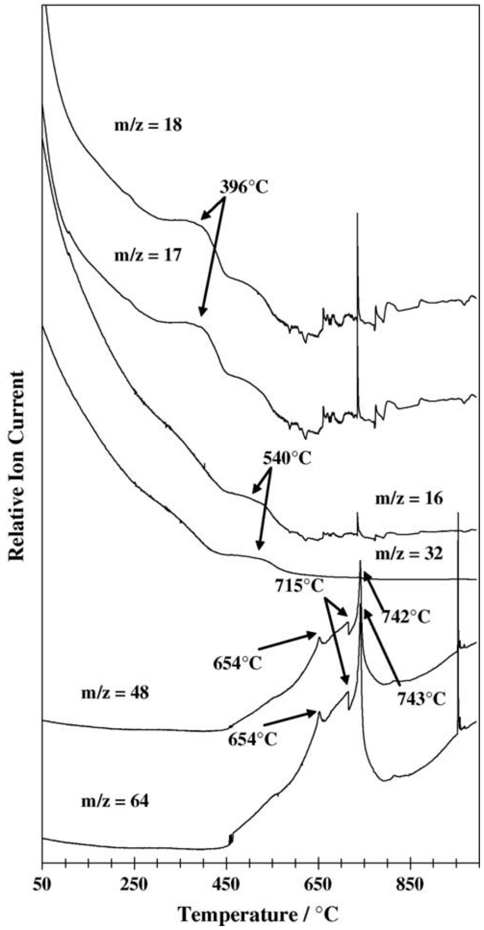

Fig. 5. Ion current curves for the evolved gases from the decomposition of sodium alunite.

The MW of Na-alunite is 398 and the % mass of OH units is 25.63%. Thus, there is 4.3% mass loss per OH unit. The mass loss at 161 and 234 °C is 5.77% which represents the loss of one and a half OH units.

Step 2b At 396 °C

$$NaO_{0.5}Al_3(SO_4)_2(OH)_5 \rightarrow NaO_2Al_3(SO_4)_2(OH)_2 + 1.5H_2O$$

The mass loss at this step is 11.25% which may be equated to the loss of three OH units. The ion current curves for the evolved gases show for $m/z = 18$ and 17 a mass gain at 396 °C. The mass gain in the MS curves corresponds precisely with the mass loss in the TG curves

Step 2c At 552 °C

$$NaO_2Al_3(SO_4)_2(OH)_2 \rightarrow NaO_3Al_3(SO_4)_2 + H_2O$$

There is a mass loss of some 33.6% which represents the mass of two OH units. The ion current curves for the evolved gases show for $m/z = 18$ and 17 a mass gain at 540 °C. The mass gain in the MS curves corresponds with the mass loss in the TG curves.

Step 3 Desulphation
Loss of sulphate

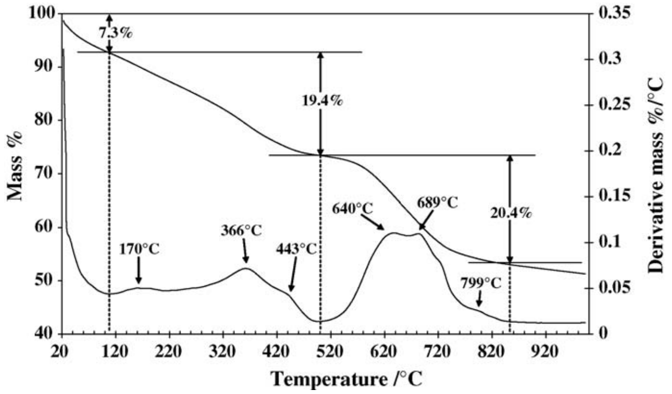

Fig. 6. Thermogravimetric analysis and differential thermogravimetric analysis of ammonium alunite.

Temperature 680 °C

$$NaO_3Al_3(SO_4)_2 \rightarrow 1/2Na_2SO_4 + SO_3 + 1.5Al_2O_3 + 2.5O_2$$

The TG and DTG curves show a large mass loss of 33.6% at 680 °C. The ion current curves for $m/z = 64$, 48 and 32 all show a peak at 682 °C confirming the loss of sulphate at this temperature.

3.4.1. Ammonium alunite

The TG/DTG curves for the thermal decomposition of NH_4-alunite are shown in Fig. 6. The ion current curves for selected evolved gases are shown in Fig. 7.

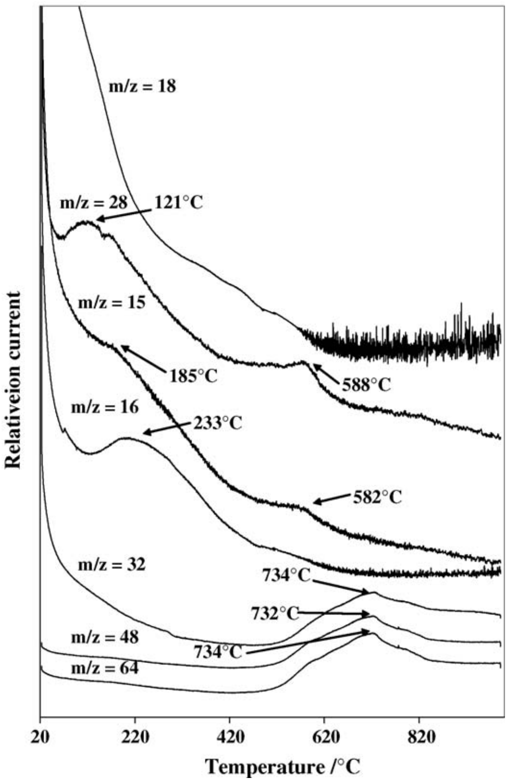

Fig. 7. Ion current curves for the evolved gases from the decomposition of ammonium alunite.

The steps in the thermal decomposition of NH_4-alunite are reported below. As for the other alunites three basic processes are involved dehydration, dehydroxylation, and desulphation. In the case of NH_4-alunite the process of de-ammoniation also occurs.

3.5. Mechanism for decomposition of ammonium alunite

Step 1 De-ammoniation
Temperature 170 °C

$$NH_4Al_3(SO_4)_2(OH)_6{\cdot}xH_2O \rightarrow HAl_3(SO_4)_2(OH)_6 + NH_3 + xH_2O$$

This step up to 170 °C involves the loss of adsorbed water and the loss of ammonia. There is a 7.31% mass loss by 100 °C. The ion current curves for $m/z = 15$, 28 show a mass gain at ~121 °C. The $m/z = 15$ curve shows that some NH_3 is retained up to 582 °C. The $m/z = 17$ is not shown as it corresponds to both NH_3 and OH, both = 17. The total mass loss for NH_3 is 4.5%. This suggests that the mass loss due to dehydration is 3.81%. It is proposed that as ammonia is lost, the ammonium ion is replaced with a proton, thus making an H-alunite (protonated alunite). There is no evidence from thermal analysis that this protonated alunite exists. However, there is some spectroscopic data that both protonated alunites and protonated jarosites cannot not only be synthesised but also exist naturally [52–56].

Step 2 Dehydroxylation

Temperature 366 and 443 °C

$$HAl_3(SO_4)_2(OH)_6 \rightarrow HAl_3O_3(SO_4)_2 + 3H_2O$$

These steps are principally the dehydroxylation steps. For the three steps at 170, 366 and 443 °C, there is a total mass loss of 21.77%. The theoretical mass loss of OH units is 25.9%.

Step 3 Desulphation
Loss of sulphate
Temperature 640, 689, 728 and 799 °C

$$2HAl_3O_2(SO_4)_2 \rightarrow 4 \cdot SO_3 + 3Al_2O_3 + H_2O$$

$$SO_3 \rightarrow SO_2 + 1/2O_2$$

Four steps are observed in the DTG curves at 640, 689, 728 and 799 °C. The ion current curves for $m/z = 64$, 48 and 32 show that sulphate is decomposing over a wide temperature range from 520 to 840 °C. The maximum for the ion current curves is at 734 °C.

4. Conclusions

The thermal decomposition of alunite is of an archeochemistry importance as alunite was used as a source of potassium. Further it has been suggested that the mineral exists on the planet Mars. If so then the wide ranging temperatures of Mars would affect the chemical composition of the alunite. Thus it is important to understand the thermal decomposition of alunite.

Alunites decompose in a series of steps based upon dehydration, dehydroxylation and desulphation. The temperatures for these processes are dependent upon the cation present. Dehydroxylation takes place in a series of three to four steps. The temperatures of the dehydroxylation show some cation dependence. Desulphation for K-alunite occurs at 680 °C, Na-alunite at 644 and 733 °C and for NH4 alunite at 640, 689 and 799 °C.

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