Thermal stability of the ‘cave’ mineral ardealite $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$

Ray L. Frost,[1] • Sara J. Palmer,[1] and Ross Pogson[2]

[1]Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[2] Mineralogy & Petrology, Australian Museum, 6 College St., Sydney, NSW, Australia 2010

Abstract

Thermogravimetry combined with evolved gas mass spectrometry has been used to characterise the mineral ardealite and to ascertain the thermal stability of this ‘cave’ mineral. The mineral ardealite $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$ is formed through the reaction of calcite with bat guano. The mineral shows disorder and the composition varies depending on the origin of the mineral. Thermal analysis shows that the mineral starts to decompose over the temperature range 100 to 150°C with some loss of water. The critical temperature for water loss is around 215°C and above this temperature the mineral structure is altered. It is concluded that the mineral starts to decompose at 125°C, with all waters of hydration being lost after 226°C. Some loss of sulphate occurs over a broad temperature range centred upon 565°C. The final decomposition temperature is 823°C with loss of the sulphate and phosphate anions.

Keywords: Raman spectroscopy, phosphate, sulphate, ardealite

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

Introduction

The mineral ardealite is known as a cave mineral and has been found in many caves worldwide [1-6]. Phosphates have been known to exist in the Jenolan Caves for a very long time [7-9]. Dating of clays in these caves suggest that the caves are very old, approximately around 350 million years [10]. It is important to know the thermal stability of this mineral, especially if it has been in existence for long periods of time. This paper addresses the issue of whether this mineral would be stable if cave temperatures were significantly high. The mineral is a mixed anion sulphate phosphate of calcium and is formed by the reaction of bat guano with calcite. The mineral is monoclinic of point group *m* and forms very thin platy crystals or powdery crusts. The mineral is intimately associated with brushite and gypsum. The formula of the mineral is given as $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$ but the composition of the mineral can vary according to the cave of origin [2-6, 10-13]. The mineral is often yellowish probably due to traces of iron in the mineral composition.

Sakae *et al.* [14] reported the crystal structure of synthetic calcium phosphate-sulfate hydrate and related the structure to brushite $CaHPO_4$ and gypsum $CaSO_4\cdot 2H_2O$. This synthesised compound proved to be monoclinic with space group *Cc*. Sakae *et al.* [14] found that the X-ray powder diffraction studies were not identical. This begs the question whether or not the synthesised compound and ardealite are identical. It is not clearly understood whether or not the structure of the synthesised compound has the same structure as the natural compound; however this seems likely. If this is the case then both the phosphate and sulphate anions occupy the C1 position. As a consequence of this symmetry all degeneracies will be removed.

Thermal analysis offers an important technique for the determination of the thermal stability of minerals [15-23]. Importantly the decomposition steps can be obtained and mechanisms of decomposition of the mineral ascertained [24-34]. There have been almost no studies of the thermal analysis of ‘cave’ minerals such as ardealite. In this research, our objective is to determine the thermal stability of the ‘cave’ mineral ardealite [4, 5, 11, 13, 35] and to assess whether the mineral is transient or stable over a wide temperature range.

Experimental

Minerals

The mineral ardealite was sourced from Moorba Cave, Jurien Bay, Western Australia, Australia. The mineral ardealite was also sourced from The Australian Museum and originated from the Jenolan caves, New South Wales, Australia. The mineral has been analysed and the data published [36]. This latter sample was used in this research. The reason for this is that spectroscopic studies indicated the sample was pure.

Thermoanalytical techniques

Thermal decomposition of ardealite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). Approximately 30 mg of sample was heated in an open platinum crucible at a rate of 5.0 °C/min up to 1000°C at high resolution. 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 selected gases such as water and sulphur dioxide were analysed. 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).

Results and Discussion

X-ray diffraction

The XRD of the ardealite before and after thermal analysis are shown in Figs 1a and 1b respectively. Fig. 1a clearly shows that the mineral sample of ardealite from the Jenolan caves is very pure with only traces of silica as tridymite detected. The XRD pattern of the products of the thermal decomposition (Fig. 1b) clearly shows that the products of the thermal decomposition are calcium sulphate and calcium phosphate.

Thermal analysis

The thermogravimetric and ion current MS patterns of the cave mineral ardealite $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$ are displayed in Figs. 2 and 3, respectively. There appear to be mass loss steps at 125, 148, around 215 and 823°C. The first two steps are attributed to the loss of adsorbed water. This attribution is confirmed by the ion current curves displayed in Fig. 2. The thermogravimetric analysis shows that the two mass loss steps at 125 and 148°C are related, as is confirmed by the ion current curves; thus it is suggested that equal amounts of water are lost in each step. It is suggested that in the structure of ardealite, two non-equivalent water molecules exist and thus are lost at two different temperatures as is evidenced by the two decomposition steps in the TG and dTG patterns. A 3.64% mass loss occurs over these two steps. The MS curves show that water is being evolved at these temperatures. These two water evolution steps are found at 125 and 150°C are attributed to adsorbed water on the surface of the mineral.

Two mass loss steps are found at 215 and 226°C with a total mass loss of 17.95%. It is suggested that the following reactions occur at these temperatures:

$Ca_2(HPO_4)(SO_4)\cdot 4H_2O \rightarrow Ca_2(HPO_4)(SO_4)\cdot 2H_2O + 2H_2O$ at ~215°C

$Ca_2(HPO_4)(SO_4)\cdot 2H_2O \rightarrow Ca_2(HPO_4)(SO_4) + 2H_2O$ at 226°C

A mass loss of 17.95% is observed over the 165 to 334°C temperature range. Ardealite has a theoretical mass of 340. The moles of water per formula unit are 4; thus the total theoretical mass loss is 20%. The measured mass loss of the first 4 mass loss steps is 3.64+17.95= 21.59%.

Over the 334 to 660°C temperature range, a mass loss of 2.96% is found. The MS curves indicate that gaseous products of sulphur are evolved at around 565°C. The MS curves are broad and provide evidence for the breakdown of the mineral as is shown by the XRD patterns (Fig. 1b). Because the mineral ardealite is found as a mineral deposit on a calcite substrate, the MS was used to check for CO_2 evolution. The MS patterns showed a gas evolution of CO_2 at 625°C resulting from the thermal decomposition of calcite.

$CaCO_3 \rightarrow CaO + CO_2$

At higher temperatures a mass loss of 13.28% is observed and is attributed to the loss of sulphur and phosphorus from the mineral. The ion current curves show that the gases of SO_2 and SO_3 are being evolved at 823°C. The mass loss of 13.28% in this high temperature range is due to a combination of decomposition reactions occurring simultaneously.

$2Ca_2(HPO_4)(SO_4) \rightarrow Ca_3(PO_4)_2 + CaSO_4 + H_2O + SO_2 + \frac{1}{2}O_2$

$Ca_3(PO_4)_2 \rightarrow 3CaO + PO_2 + PO + O_2$

$2Ca(SO_4) \rightarrow 2CaO + SO_2 + SO + 1\frac{1}{2}O_2$

Conclusions

The mineral ardealite is known as a ‘cave’ mineral and is found in many caves worldwide. Experiments were conducted to test the stability of the mineral and to find over what temperature range the mineral is stable. Thermal analysis shows that the mineral starts to decompose at low temperatures and the decomposition range occurs over the temperature range 125 to 150°C with some loss of water. The critical temperature for water loss is around 215°C and above this temperature the mineral structure is altered. Some loss of sulphate occurs over a broad temperature range centred upon 565°C. It is concluded that the mineral starts to decompose at 125°C and all waters of hydration are lost by 226°C. The structural integrity of the mineral above this temperature is lost as is shown by the XRD patterns of the products of the thermal decomposition.

Acknowledgments

The financial and infra-structure support of the Queensland University of Technology, Chemistry Discipline is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

References

[1] D.-G. Dumitras, S. Marincea, E. Bilal, F. Hatert, Apatite-(CaOH) in the fossil bat guano deposit from the "dry" Cioclovina Cave, Sureanu Mountains, Romania,Canadian Mineralogist 46 (2008) 431-445.

[2] C. A. Hill, Cave Minerals, 1976.

[3] D. Moravansky, M. Orvosova, Recent knowledge about the cave minerals of Slovakia,Mineralia Slovaca 39 (2007) 203-216.

[4] D. Moravansky, P. Zenis, Guano minerals in some caves of Western and Central Slovakia,Mineralia Slovaca 29 (1997) 61-72.

[5] B. P. Onac, J. E. Mylroie, W. B. White, Mineralogy of cave deposits on San Salvador Island, Bahamas,Carbonates and Evaporites 16 (2001) 8-16.

[6] W. B. White, Cave minerals and speleothems,Sci. Speleol. (1976) 267-327.

[7] J. C. H. Mingaye, Phosphatic deposits in the Jenolan Caves, N. S. Wales,Rept. Australian Assoc. 7 (1898) 111-116.

[8] J. C. H. Mingaye, Phosphatic deposits in the Jenolan Caves, N. S. Wales,Records Geol. Survey N.S. Wales 6 (1899) 111-116.

[9] C. A. Suessmilch, W. G. Stone, Geology of the Jenolan caves district,Journal and Proceedings of the Royal Society of New South Wales 49 (1916) 332-384.

[10] R. a. L. Osborne, H. Zwingmann, R. E. Pogson, D. M. Colchester, Carboniferous clay deposits from Jenolan Caves, New South Wales: implications for timing of speleogenesis and regional geology,Australian Journal of Earth Sciences 53 (2006) 377-405.

[11] D.-G. Dumitras, S. Marincea, A.-M. Fransolet, Brushite in the bat guano deposit from the "dry" Cioclovina Cave (Sureanu Mountains, Romania),Neues Jahrbuch fuer Mineralogie, Abhandlungen 180 (2004) 45-64.

[12] C. A. Hill, Recent anhydrite and bassanite from caves in Big Bend National Park, Texas,NSS Bulletin 41 (1979) 126-127.

[13] I. Shopov, Bulgarian cave minerals,NSS Bulletin 50 (1988) 21-24.

[14] T. Sakae, H. Nagata, T. Sudo, The crystal structure of synthetic calcium phosphate-sulfate Ca2hPO4SO4.4H2O,American Mineralogist 63 (1978) 520-527.

[15] H. Cheng, J. Yang, R. L. Frost, Q. Liu, Z. Zhang, Thermal analysis and Infrared emission spectroscopic study of kaolinite-potassium acetate intercalate complex,J. Therm. Anal. Calorim. 103 (2011) 507-513.

[16] S. J. Palmer, L. M. Grand, R. L. Frost, Thermal analysis of hydrotalcite synthesised from aluminate solutions,J. Therm. Anal. Calorim. 103 (2011) 473-478.

[17] K. H. Bakon, S. J. Palmer, R. L. Frost, Thermal analysis of synthetic reevesite and cobalt substituted reevesite (Ni,Co)6Fe2(OH)16(CO3) Â· 4H2O,J. Therm. Anal. Calorim. 100 (2010) 125-131.

[18] R. L. Frost, S. Bahfenne, Thermal analysis and Hot-stage Raman spectroscopy of the basic copper arsenate mineral,J. Therm. Anal. Calorim. 100 (2010) 89-94.

[19] R. L. Frost, S. J. Palmer, L.-M. Grand, Synthesis and thermal analysis of indium-based hydrotalcites of formula Mg6In2(CO3)(OH)16·4H2O,J. Therm. Anal. Calorim. 101 (2010) 859-863.

[20] R. L. Frost, S. J. Palmer, J. Kristof, E. Horvath, Dynamic and controlled rate thermal analysis of halotrichite,J. Therm. Anal. Calorim. 99 (2010) 501-507.

[21] R. L. Frost, S. J. Palmer, J. Kristof, E. Horvath, Thermoanalytical studies of silver and lead jarosites and their solid solutions,J. Therm. Anal. Calorim. 101 (2010) 73-79.

[22] L.-M. Grand, S. J. Palmer, R. L. Frost, Synthesis and thermal stability of hydrotalcites containing manganese,J. Therm. Anal. Calorim. 100 (2010) 981-985.

[23] L.-M. Grand, S. J. Palmer, R. L. Frost, Synthesis and thermal stability of hydrotalcites based upon gallium,J. Therm. Anal. Calorim. 101 (2010) 195-198.

[24] J. Kristof, R. L. Frost, S. J. Palmer, E. Horvath, E. Jakab, Thermoanalytical studies of natural potassium, sodium and ammonium alunites,J. Therm. Anal. Calorim. 100 (2010) 961-966.

[25] L. Lu, J. Cai, R. L. Frost, Desorption of stearic acid upon surfactant adsorbed montmorillonite,J. Therm. Anal. Calorim. 100 (2010) 141-144.

[26] L. Lu, R. L. Frost, J. Cai, Desorption of benzoic and stearic acid adsorbed upon montmorillonites: a thermogravimetric study,J. Therm. Anal. Calorim. 99 (2010) 377-384.

[27] S. J. Palmer, R. L. Frost, Thermal decomposition of Bayer precipitates formed at varying temperatures,J. Therm. Anal. Calorim. 100 (2010) 27-32.

[28] Q. Tao, H. He, R. L. Frost, P. Yuan, J. Zhu, Thermal decomposition of silylated layered double hydroxides,J. Therm. Anal. Calorim. 101 (2010) 153-159.

[29] J. Yang, R. L. Frost, W. N. Martens, Thermogravimetric analysis and hot-stage Raman spectroscopy of cubic indium hydroxide,J. Therm. Anal. Calorim. 100 (2010) 109-116.

[30] R. L. Frost, M. C. Hales, W. N. Martens, Thermogravimetric analysis of selected group (II) carbonate minerals. Implication for the geosequestration of greenhouse gases,J. Therm. Anal. Calorim. 95 (2009) 999-1005.

[31] R. L. Frost, J. Kristof, E. Horvath, Controlled rate thermal analysis of sepiolite,J. Therm. Anal. Calorim. 98 (2009) 423-428.

[32] S. J. Palmer, J. Kristof, V. Vagvoelgyi, E. Horvath, R. L. Frost, Thermal decomposition of hydrotalcite with hexacyanoferrate(II) and hexacyanoferrate(III) anions in the interlayer,J. Therm. Anal. Calorim. 96 (2009) 449-454.

[33] N. Voyer, A. Soisnard, S. J. Palmer, W. N. Martens, R. L. Frost, Thermal decomposition of the layered double hydroxides of formula Cu6Al2(OH)16CO3 and Zn6Al2(OH)16CO3,J. Therm. Anal. Calorim. 96 (2009) 481-485.

[34] V. Vagvoelgyi, M. Hales, R. L. Frost, A. Locke, J. Kristof, E. Horvath, Conventional and controlled rate thermal analysis of nesquehonite Mg(HCO3)(OH)Â·2(H2O),J. Therm. Anal. Calorim. 94 (2008) 523-528.

[35] B. P. Onac, J. W. Hess, W. B. White, The relationship between the mineral composition of speleothems and mineralization of breccia pipes: evidence from corkscrew cave, Arizona, USA,Canadian Mineralogist 45 (2007) 1177-1188.

[36] J. W. Anthony, R. A. Bideaux, K. W. Bladh, M. C. Nichols, Handbook of Mineralogy, Mineral Data Publishing, Tuscon, Arizona, USA, 2000.

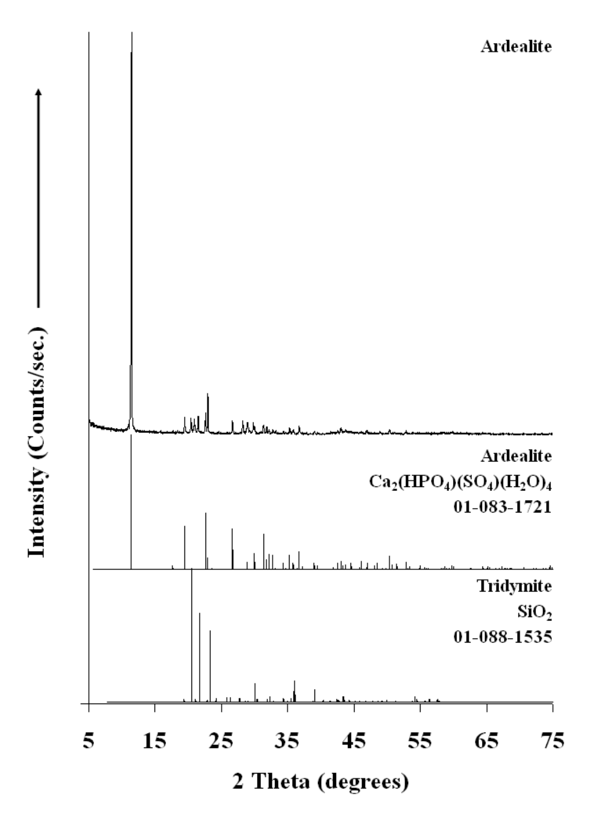

Figure 1a

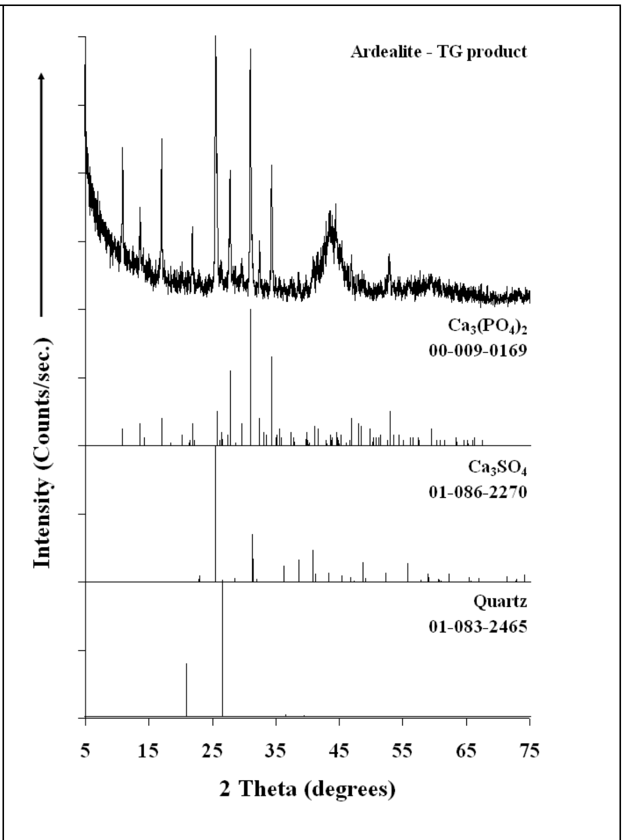

Figure 1b

List of Figures

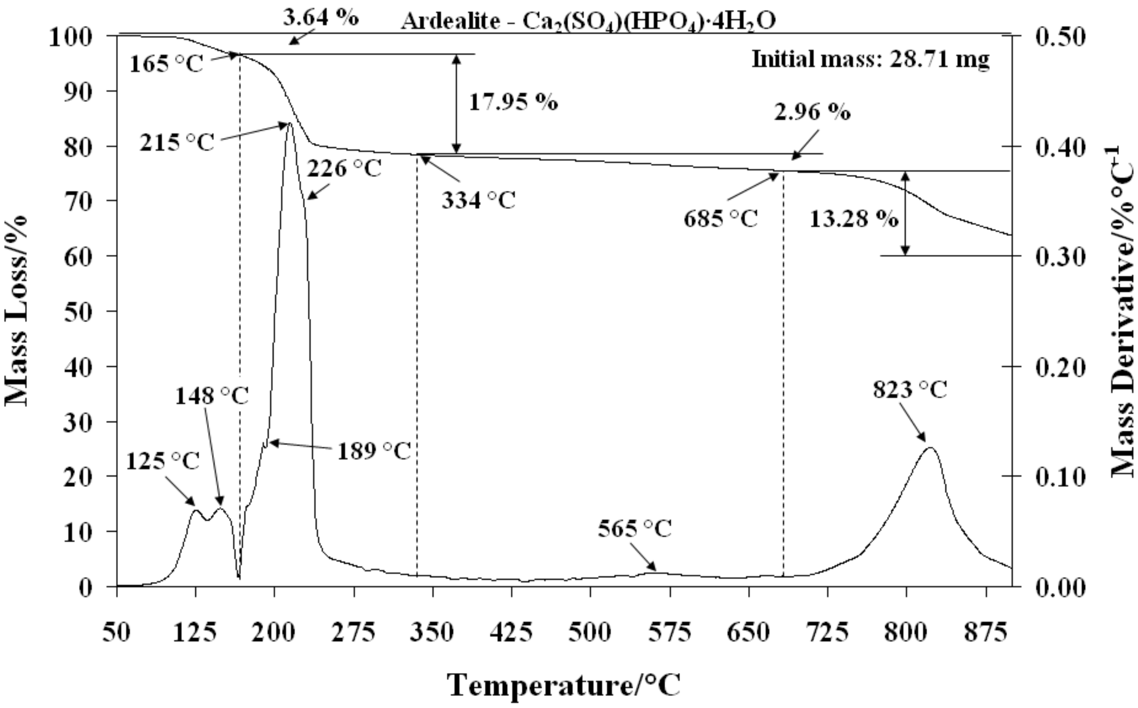
Ardealite - $Ca_2(SO_4)(HPO_4)\cdot 4H_2O$
Initial mass: 28.71 mg
3.64 %
17.95 %
2.96 %
13.28 %
165 °C
215 °C
226 °C
334 °C
685 °C
148 °C
125 °C
189 °C
565 °C
823 °C
Mass Loss/%
Mass Derivative/%°C^{-1}
Temperature/°C
100
90
80
70
60
50
40
30
20
10
0
0.50
0.40
0.30
0.20
0.10
0.00
50
125
200
275
350
425
500
575
650
725
800
875

Figure 2

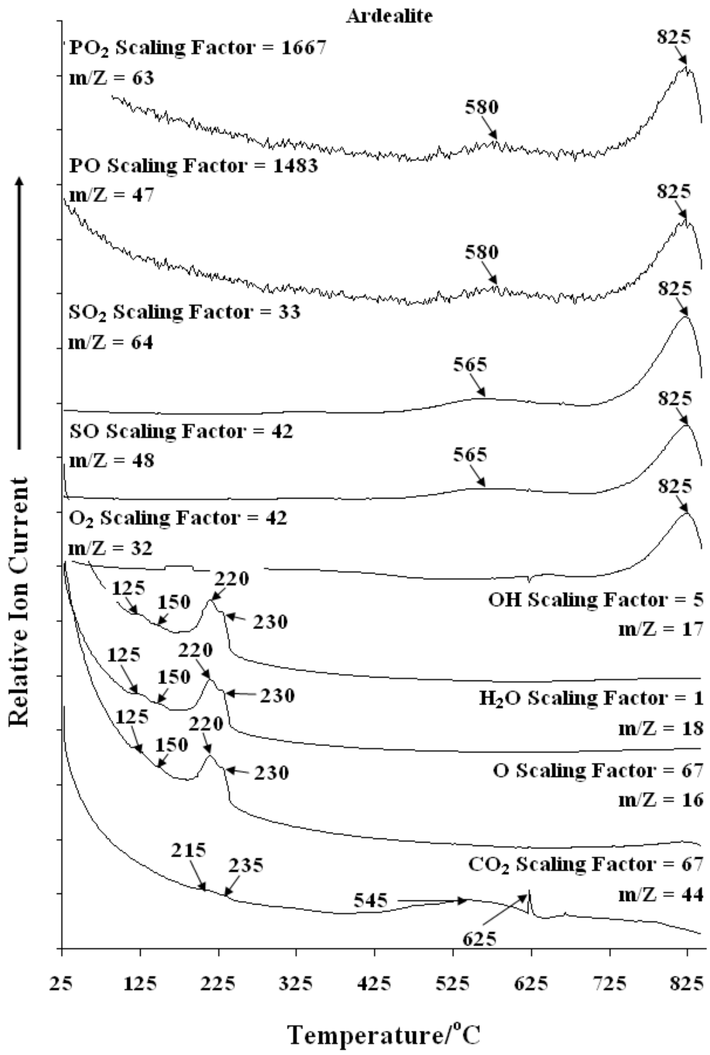
Ardealite
PO2 Scaling Factor = 1667
m/Z = 63
825
580
PO Scaling Factor = 1483
m/Z = 47
825
580
SO2 Scaling Factor = 33
m/Z = 64
825
565
SO Scaling Factor = 42
m/Z = 48
825
565
O2 Scaling Factor = 42
m/Z = 32
825
125
150
220
230
OH Scaling Factor = 5
m/Z = 17
125
150
220
230
H2O Scaling Factor = 1
m/Z = 18
125
150
220
230
O Scaling Factor = 67
m/Z = 16
215
235
545
625
CO2 Scaling Factor = 67
m/Z = 44
Relative Ion Current
25
125
225
325
425
525
625
725
825
Temperature/°C

Figure 3