

# Thermal decomposition of agardites (REE)—relationship between dehydroxylation temperature and electronegativity

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## Abstract

The thermal decomposition of a suite of synthetic agardites of formula  $ACu_6(AsO_4)_2(OH)_6 \cdot 3H_2O$  where A is given by a rare earth element has been studied using thermogravimetric analysis techniques. Dehydration of the agardites occurs at low temperatures and over an extended temperature range from ambient to around 60 °C. This loss of water is attributed to the loss of zeolitic water. The mass loss of water indicates 3 mol of zeolitic water in the structure. Dehydroxylation occurs in steps over a wide range of temperatures from 235 to 456 °C. The mass loss during dehydroxylation shows the number of moles of hydroxyl units is six. There is a linear relationship between the first dehydroxylation temperature and the electronegativity of the agardites (REE).

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## 1. Introduction

Mixites are a group of minerals which are found in different parts of the world [1–7]. Several of these minerals are found in Australia [8]. Mixites are hexagonal arsenates and phosphates of the general formula  $ACu_6(As,PO_4)_2(OH)_6 \cdot 3H_2O$ . Agardite is a member of the mixite group,  $ACu_6(AsO_4)_2(OH)_6 \cdot 3H_2O$  for the fully hydrated formula, with (A = REE<sup>3+</sup>). Mixite (A = Bi), goudeyite (A = Al), zalesiite (A = Ca, with protonation of the lattice for charge compensation) and petersite-(Y), the phosphate analogue of agardite-(Y) are recognized as isomorphous species in the group. Water in the lattice is for the most part thought to be zeolitic in nature, as evidenced by single-crystal X-ray structure determinations [8–10]. The crystal structures of natural mixite and agardite compounds reveal a microp-

orous framework structure [9,11] with a framework similar to that of zeolites [10]. Dietrich et al. proposed that the water in agardite was zeolitic [12]. As such these types of minerals may have the potential for catalytic applications. The mixite group consists of secondary minerals formed through crystallisation from aqueous solution. The conditions under which this crystallisation takes place, particularly relating to anion and cation concentration, pH, temperature and kinetics of crystallisation, determines the particular mineral that is formed. Recently, thermal analysis has been used to gain an understanding of many properties of secondary minerals [13–17]. In particular, high-resolution thermogravimetric analysis has been used to determine paragenetic relationships between many closely related phases [13].

Several authors have commented upon the nature of the water of hydration in mixite group minerals. It has been found that the water is zeolitic in nature and exhibit reversible hydration behaviour. It was considered necessary, therefore, to determine the degree of hydration in the agardite group miner-

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als produced synthetically. In this paper, we report the HRTG and dTG of a set of synthetic agardite minerals and a relationship involving the mass loss parameters and the electronegativities of the agardites of the agardites (REE) elements.

## 2. Synthesis of agardites

Pure end-members of the agardite group were synthesized in the following way. To 30 cm<sup>3</sup> of water in a 250 cm<sup>3</sup> teflon-lined acid digestion bomb was added with stirring 6.0 mmol of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, 3.0 mmol of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, and 1.0 mmol of Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The pH of the mixture was adjusted to 6.6 by dropwise addition of 1.0 M aqueous NaOH. The bomb was sealed and the mixture heated at 180 °C for 48 h, then cooled to room temperature. The product, agardite-(Y), was filtered off, washed with water, then acetone and sucked dry at the pump (yield > 95%). Powder X-ray diffraction using a Phillips PW1825 X-ray diffractometer with Mo K $\alpha$  radiation showed that a single crystalline phase was present. Separate pure samples of agardite-(La), -(Ce), -(Pr), -(Nd), -(Sm) and -(Eu) were prepared in identical fashion with similar yields by substituting the appropriate hydrated REE nitrate for Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. A single phase was present.

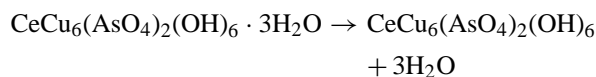
### 2.1. Thermal analysis

Thermal decomposition of the agardite was carried out in a TA<sup>®</sup> Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm<sup>3</sup>/min). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 2.0 °C/min up to 800 °C. The instrument was operated with resolution of 8. The number 8 is an arbitrary number and represents the highest resolution with the number 1 being the lowest. The significance of this value is that the analyses occur over extended periods of time up to 2 days. 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 were analyzed.

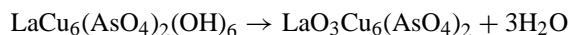
## 3. Results and discussion

The result of the TGA analyses, given in Table 1, show that the synthetic agardites are all fully hydrated, i.e.,  $n = 3$ . The fact that in all cases the number of waters calculated is greater than three is either a result of the presence of a small quantity of adsorbed water in the products or partial decomposition of arsenate, AsO<sub>4</sub><sup>3-</sup>, to pyroarsenate, As<sub>2</sub>O<sub>7</sub><sup>4-</sup>.

The thermogravimetric and differential thermogravimetric curves for the agardites of La are shown in Fig. 1. The Thermogravimetric patterns of Ce, Sm, Pr, Y and Eu are similar. In all of the patterns, there is an initial mass loss of between 5.6 and 6%. This mass loss occurs over the temperature range between ambient and 70 °C. Ion current analysis of the evolved gases confirms the water loss. This mass loss is attributed to the loss of zeolitic water. If we use the formula CeCu<sub>6</sub>(AsO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O for the Ce agardite, the theoretical mass loss for 3 mol of water is 5.65 %. Thus, the experimental mass loss of water is in good agreement with the theoretical value. It should be recognised that the amount of water in the agardite structure is variable [10]. It is proposed that the loss of water is given by:



For agardite (La) several mass loss steps are observed at temperatures of 235, 294, 370, 419 and 443 °C. These mass loss steps are assigned to the dehydroxylation of the agardite (La). It is apparent that dehydroxylation of the agardite (La) occurs over a wide temperature range. The total mass loss for agardite (La) over all the dehydroxylation steps is 5.4%. The theoretical mass loss based upon the formula CeCu<sub>6</sub>(AsO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O is 5.65 %. Thus, the experimental result is in good agreement with the theoretical value. It is suggested that the reaction for the dehydroxylation of the agardite (La) is given by:



The formula for the thermally decomposed agardite (La) is given as LaO<sub>3</sub>Cu<sub>6</sub>(AsO<sub>4</sub>)<sub>2</sub>. It is not known but may be a mixture of oxides and arsenates. For agardite (Ce), dehydroxylation temperatures are observed at 305, 439 and 454 °C with a total mass loss due to dehydroxylation of 4.8%. For agardite (Sm), two dehydroxylation temperatures are ob-

Table 1  
Results of the thermogravimetric analyses of agardites

Element	Water loss		No. of waters	Dehydroxylation 1		Dehydroxylation 2	
	(°C)	(%)		(°C)	(%)	(°C)	(%)
La	<100	5.99	3.69	235–294	1.1	370–419	4.3
Ce	<100	5.85	3.61	305	1.3	439–454	3.5
Pr	<100	6.2	4.36	295	0.3	384–443	4.2
Sm	<100	5.95	4.17	381	0.8	433	3.4
Eu	<100	5.51	3.42	377	0.8	437	3.5
Y	<100	5.32	3.10	372	1.0	423–456	4.2

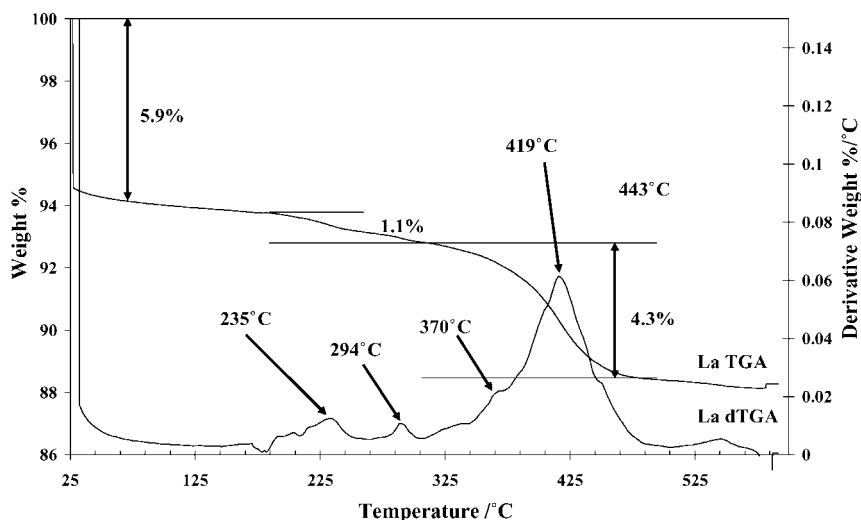


Fig. 1. TG and DTG curves of agardite (La).

served at 381 and 433 °C with a total mass loss of 4.2%. For agardite (Pr) dehydroxylation temperatures of 295, 384, 415, 426 and 443 °C are observed with a total mass loss of 4.2%.

It is possible to propose a relationship between the first dehydroxylation temperature and the electronegativity (using the Pauling scale of electronegativities) of the REE in the agardite. This is illustrated in Fig. 2. The relationship is given by  $y = 1169.8x - 1021.7$  with an  $R^2$  value of 0.78. It is apparent that there is a linear relationship between the first dehydroxylation temperature and the electronegativity of the REE. An attempt was made to correlate the first dehydroxylation temperature with reciprocal ionic radius. However, the relationship was not as good as for electronegativity. The reason why there is an apparent relationship between the dehydroxylation temperature and electronegativity is related to the bond strength of the OH units and the REE. This bond strength is affected by the electronegativity.

Infrared spectra of the hydroxyl-stretching region for the rare earth element agardites show close similarities. In  $\text{REECu}_6(\text{AsO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , OH units and water will contribute to the overall spectroscopic profile. Four OH stretching bands are observed at around 3568, 3482, 3362 and  $3296\text{ cm}^{-1}$ . The band at  $3568\text{ cm}^{-1}$  is constant within experimental error for all synthesised agardites, but the band at  $3296\text{ cm}^{-1}$  shows considerable variation in position. It is apparent that the position of the band is agardite-element dependent. The band at  $<3300\text{ cm}^{-1}$  is assigned to the OH stretching vibration of water. The position of this band suggests that the water is quite strongly hydrogen bonded. It may be reversibly removed from the lattice by heating, but it is certainly strongly structured water. Studies have shown a strong correlation between OH stretching frequencies and both O...O bond distances and H...O hydrogen bond distances [18–21]. Libowitzky (1999) based upon the

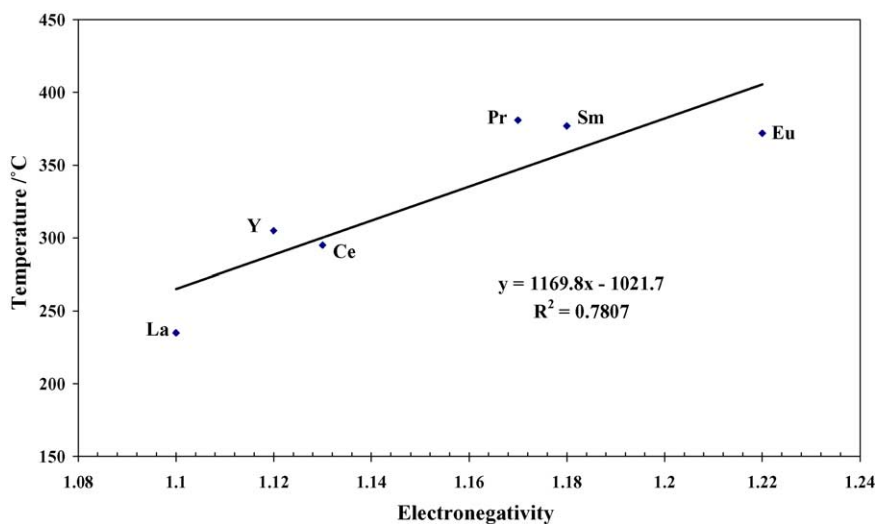


Fig. 2. Relationship between the first dehydroxylation temperature and electronegativity of the REE agardite.

hydroxyl stretching frequencies as determined by infrared spectroscopy, showed that a regression function can be employed relating the above correlations with regression coefficients better than 0.96 [22]. Calculation shows that a wavelength of  $3240\text{ cm}^{-1}$  corresponds to a hydrogen bond distance of approximately  $2.72\text{ \AA}$ . The O–H...O bond distances in ice is  $2.77\text{ \AA}$ . In other words the hydrogen-bonded water in the mixite channels for some congeners is more strongly hydrogen bonded than is the case with ice. In comparison, the band at  $\sim 3568\text{ cm}^{-1}$  is assigned to non-hydrogen bonded water and in this case calculations show the O–H...O bond distance is about  $3.07\text{ \AA}$ . This type of water is space-filling water. This may be described as the zeolitic water. Thus infrared spectroscopy indicates two types of water in agardites namely highly structure water and zeolitic water. It is probable that an increase in electronegativity causes the OH bond to weaken as hydrogen bonding becomes more significant. There are several possible explanations for this. In the structure of agardite, the hydroxyl groups are bonded to Cu. As electronegativity increases, more electrons are withdrawn from Cu, causing the OH bond to strengthen. Another explanation is that higher electronegativity is linked to a smaller ionic radius. The decrease in radius results in a smaller unit cell size and strengthens the OH bond.

#### 4. Conclusions

Thermogravimetry and differential thermogravimetry have been used to study the thermal decomposition of a series of synthetic REE agardites. Dehydration occurs from ambient to around  $60\text{ }^\circ\text{C}$  with the loss of 3 mol of water attributed to zeolitic water in the channels of the agardite structure. Dehydroxylation is lanthanide element dependent and the first dehydroxylation temperature is an apparent linear function of the REE electronegativity.

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