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Heating Effects in the Structure of Non-metamict Allanite-(La) from Palawan, Philippines

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Allanite is one of the most common sources of rare-earth elements (REEs) and contains significant amounts of thorium (Th) and uranium (U). The presence of radioactive Th and U nuclides in the mineral exposes it to long-term radiation. Like other natural minerals containing Th and U, allanite can be used as a natural analog to understand the long-term radiation effects in high-level nuclear waste (HLW) matrices. Allanite group mineral is generally found in the amorphous phase due to structural damage induced by self-irradiation. In this work, crystalline allanite-(La) samples collected in San Vicente, Palawan, Philippines – having a low absorbed dose of $\sim 10^{14}$ α -decays/mg – were heated at 450, 650, and 850 °C to study the response of non-metamict allanite to heating at elevated temperatures, particularly at the early stages of exposure to alpha-particle radiation. An increase in structural order was observed upon heating to 450 and 650 °C, which is exhibited by a decrease in the unit cell volume by 1.6% and a decrease of the full width at half maximum (FWHM) of selected Bragg planes. It was evident that certain Bragg planes respond differently to the annealing temperatures with preferential reorientation. After annealing at 850 °C, however, the loss of OH bonds was observed in the infrared (IR) spectra, and the broadening of Bragg peaks was seen in the x-ray diffraction (XRD) patterns, suggesting an onset of structural degradation. Surface cracks are also seen in the scanning electron microscope (SEM) images. The study shows that the non-metamict allanite-(La) mineral structure responds to heating similarly to that of metamict ones reported in the literature. This study will provide data on the properties of allanite as part of the ongoing studies on radiation damage in silicate matrices.

Keywords: absorbed α -dose, allanite, heating, FTIR, XRD

INTRODUCTION

Allanite belongs to the sorosilicates with monoclinic $P2_1/m$ symmetry and is represented by the general formula $(Ca, REE)_2(Al, Me)_3(SiO_4)(Si_2O_7)O(OH)$, where the

REE contains REEs (Th and U) and the Me sites are occupied by trivalent and divalent cations such as Fe^{3+} , Fe^{2+} , Mn^{3+} , and Mg^{2+} (Dollase 1971; Ercit 2002; Gieré and Sorensen 2004). The allanite group minerals have been found to be a good candidate as a natural analog for REE- and actinide-bearing HLW in a silicate matrix (Sengupta and Kale 2005). The monoclinic structure of

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allanite can incorporate elements with varying substitution mechanisms (Spürgrin *et al.* 2009) ranging from more than 25 wt% of REEs occupying the cation sites (Beirau *et al.* 2011). It can also incorporate Th and U elements ranging from 0.05–3 wt% and 10–3000 ppm, respectively (Gieré and Sorensen 2004; Beirau 2012). The allanite group mineral, depending on the chemical composition, has the unit cell parameters: $a = 8.9\text{--}9.0\text{ \AA}$, $b = 5.7\text{--}5.8\text{ \AA}$, $c = 10.1\text{--}10.2\text{ \AA}$, and $\beta = 114.8\text{--}116.0^\circ$ (Paulmann and Bismayer 2001; Beirau *et al.* 2011). The allanite has four general species – allanite-(La), allanite-(Ce), allanite-(Y), and, rarely, allanite-(Nd) – depending on the most abundant REE present in the mineral.

The presence of the radioactive elements Th and U in allanite makes it an appropriate natural analog for studying the long-term effects of self-irradiation in nuclear waste disposal material. The mineral's crystal structure can be destroyed as a result of the radioactive α -decay events of Th and U plus their daughter products. Generally, radiation damage in minerals results from the interaction of α -particles and the recoil nuclei within the mineral's crystal structure after a radioactive decay. Mineral structures expand in response to radiation damage (Janeczek and Eby 1993). The extent of the radiation effect in the mineral's crystalline structure is dependent on the α -radiation dose (Malczewski and Grabias 2008; Lumpkin *et al.* 2014). The absorbed α -dose is dependent on the amount of radionuclides – U and Th – inherently present and the mineral's geological age. Hence, the same mineral species may occur in the crystalline phase, a mixture of aperiodic and crystalline regions, or a completely amorphous or metamict phase. Allanite is generally found in nature in a metamict or partially-metamict state (Čobić *et al.* 2010; Beirau *et al.* 2011). Apart from the radionuclides present in the mineral, Čobić *et al.* (2010) suggested that the vast amounts of substitution of cations with different ionic radii and charges in the mineral induce instability in the crystal structure and favors the metamictization process.

The heating of a “perfect” crystalline mineral at high temperatures leads to the formation of a large number of thermally induced lattice defects. At elevated temperatures, the defects such as dislocations can interact with other defects to remove or form more intricate defect structures (Schwartz and Lang 2016). Likewise, the heating of the metamict allanite at very high temperatures breaks down its crystal structure and increases structural/lattice defects. However, heating at an appropriate temperature recovers their crystal structure and decreases the number of structural/lattice defects.

Several studies have investigated the behavior of radiation-damaged allanite by subjecting it to increased temperature to reverse the metamictization. Janeczek and

Eby (1993) observed the start of partial recrystallization of amorphous allanite between 500–600 °C. Čobić *et al.* (2010) found that partial recrystallization of allanite-(Ce) occurred at 650 °C, followed by structural decomposition at higher temperatures. On the other hand, recrystallization under hydrothermal conditions leads to a quicker and complete annealing process, even at lower temperatures. Beirau *et al.* (2011) induced recrystallization of radiation-damaged allanite at 800–850 °C and found that heating at ~ 1000 °C destroyed its crystal completely. Bonazzi and Menchetti (1994) showed a significant increase in the unit cell parameter along the c-axis in the annealing experiments in the air at 700–800 °C and structure began to break down between 905–930 °C.

Up to now, however, very little is known about the response of non-metamict allanite to heating at elevated temperatures. Since allanites have varying elemental compositions, REE content, and extent of radiation damage, this study hopes to present heating effects in allanite samples from San Vicente, Palawan, Philippines, which are non-metamict and are relatively young. It has an estimated geologic age of 24–35 Ma and acquired an absorbed α -dose of 2.84×10^{14} α -decays/mg (Dingle *et al.* 2019). Given that the allanite has been exposed to an amount of α -radiation across geological timescales, it is assumed that there will be the presence of localized damage within the crystal structure and heating may improve the localized damage, hence this work. This study will provide data on the properties of allanite as part of the ongoing studies on radiation damage in silicate matrices, particularly at the early stages of exposure to alpha-particle radiation. Since HLW releases heat during the decay process, this work may also have implications on the properties or processes useful in characterizing the area of the deposit in the future and the behavior of radioactive waste in a silicate matrix when disposed and buried underground.

MATERIALS AND METHODS

Sample Description

The samples of allanite-(La) minerals were collected from the downstream sands in Ombo, San Vicente, Palawan, Philippines. The source of the allanite-(La) was found to be from the granitic rock of Mt. Kapoas (Padrones *et al.* 2017). The allanite-(La) found in this area, shown in Figure 1, appears as brownish to brownish-black, glassy, and slightly elongated grains with sizes ranging from 1–4 mm.

The allanite-(La) was previously characterized by Dingle *et al.* (2019) for elemental, radiometric, and structural properties using x-ray fluorescence spectrometry, gamma-

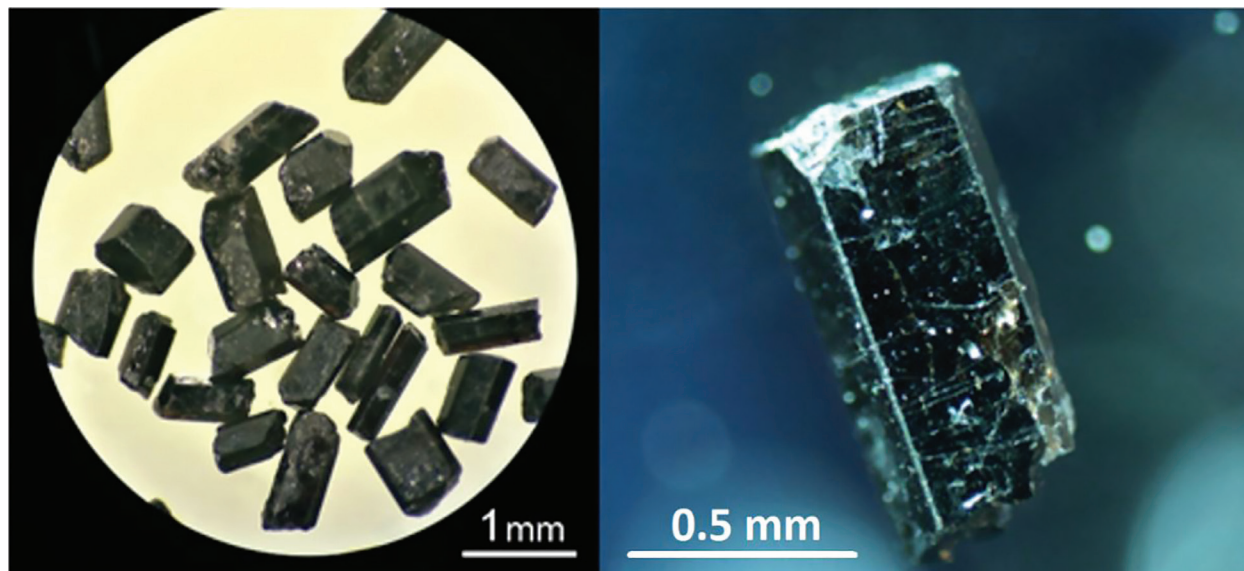


Figure 1. Allanite grains as viewed from a Leica EZ4 stereomicroscope with ~200x magnification.

ray spectrometry, and XRD, respectively. Radiometric dating using gamma-ray spectrometry estimated the age of the allanite mineral to be around 24–35 million years. The allanite sample contains 1.37 wt% ThO₂ and ~30.4 wt% REE oxides (Y, La, Ce, Pr, Nd, and Sm). Ce (CeO₂) has the highest concentration among the REE oxides amounting to 15.26 wt%, followed by La (La₂O₃) with 7.69 wt%. The x-ray diffractogram of the allanite-(La) showed that it still exhibited a highly crystalline structure, even after it had acquired an absorbed α -dose of 2.84×10^{14} α -decays/mg.

Sample Collection and Preparation

Bulk sample collection and allanite mineral separation were described in a study by Dingle *et al.* (2019). Pulverized grains were heated in a furnace for 1 h at 450, 650, and 850 °C in atmospheric conditions. The annealing period was chosen based on Janeczek and Eby (1993), who reported that the profound changes in the crystallinity of metamict allanite occur within the first 1 h of heating. The heated samples were then cooled to room temperature and characterized using FTIR (Fourier-transform infrared spectroscopy), XRD, and SEM.

Experimental

The morphology of the allanite grains was observed using the SigmaTech Hitachi Model TM 3000 SEM before and after heating at 850 °C. The SEM filament was operated at 5 and 15kV with 300–1000 $\times$ magnification. The infrared spectra of the untreated and heated allanite were collected using a Shimadzu Prestige 21 FTIR Spectrometer in attenuated total reflectance (ATR) mode

with the Miracle ATR single reflectance of the Pike Technologies spectrometer. The measurements were taken in the range of 400–4000 cm⁻¹ at an instrumental resolution of 0.5 cm⁻¹ (mid/far-IR) and 2 cm⁻¹ (near-IR) at room temperature.

The untreated and heated allanite samples were smeared in the glass substrates prior to XRD analysis. The diffractograms were obtained using the Xpert Pro Diffractometer system (Cu-K α , λ = 1.54 Å) with a step size of 0.07° and a rate of 37.48 s per step at a fixed divergence slit of 0.76 mm. It was operated at 45 kV and 40 mA from 2 θ angles of 10–60°. The resulting XRD pattern of the untreated sample was manually compared with several allanite patterns of the International Center for Diffraction Data database to determine the allanite species and further verified using the Match! phase identification software version 3.5.1. The lattice parameters of each sample were calculated analytically using the indexed (*hkl*) planes (001), (100), (020), and (201) plus their corresponding d-spacing values using Equation 1 (Cullity and Stock 2001).

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hlc\cos\beta}{ac} \right) \quad (1)$$

From the identified lattice parameters, the unit cell volume (*V*) was calculated using Equation 2 and compared with a pristine allanite sample.

$$V = abc \sin\beta \quad (2)$$

RESULTS

FTIR Analysis

Figure 2 shows the FTIR spectra of the untreated allanite sample and annealed at 450, 650, and 850 °C. The spectrum in the 1200–550 cm^{-1} range consists of five absorption bands present at 1042, 921, 880, 635, and 576 cm^{-1} . The observed vibration modes are tabulated in Table 1. The bands observed at 550–700 cm^{-1} corresponding to Si-O tilting modes appeared to be almost unaffected by heating as there were no observed changes in the spectra along this region upon heating up to 650 °C. However, peak intensity decreased upon heating at 850 °C, suggesting that the structure has been degraded.

In this study, the Si-O stretching band at 1042 cm^{-1} of the allanite-(La) was observed at a higher wavenumber compared to the allanite-(La) (1035–1004 cm^{-1}) that was studied by (Hoshino *et al.* 2005), who observed a shift

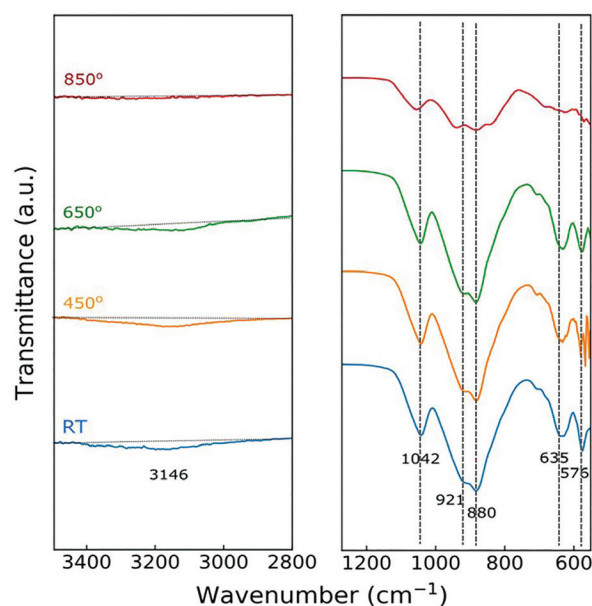


Figure 2. FTIR spectra of allanite at room temperature and after annealing at 450, 650, and 850 °C.

Table 1. Absorption bands, band ranges (shown in parenthesis), and corresponding intensities seen in untreated Ombo allanite-(La) sample.

IR bands	Absorption bands (cm^{-1})	Absorption intensity
Si-O tilting	576, 635 (550–700)	Weak
Si-O tetrahedral stretching	880, 921, 1042 (780–1100)	Strong

towards the lower wavenumber with increasing damage. This band slightly increased when the sample was heated at 450 °C. The two bands in the 880–950 cm^{-1} range still corresponding to the Si-O stretching band are seen even in the untreated sample. These intense bands are narrow, resembling the spectra of fully crystalline allanite (Beirau 2012; Janeczek and Ebby 1993), suggesting that no damage to the crystal phase has yet occurred in the mineral that may cause metamictization. Although this was the case, high-temperature treatment of allanite might have an important effect on its physical and mechanical characteristics, which plays an important role in nuclear waste disposal (Sun *et al.* 2016); hence, further heating of the allanite was conducted. Heat treatment of the crystalline allanite to 850 °C leads to a decrease in the intensity, less sharp peaks, and broadening of the Si-O tilting mode absorption bands – lying between 550–700 cm^{-1} and the Si-O stretching mode between 880–1100 cm^{-1} . This observation might be attributed to the re-positioning of the atoms, leading to the ordering of the crystal lattice as confirmed by the XRD results.

Further, the stretching modes of the structural hydroxide groups (O-H) between 2800–3400 cm^{-1} , which seems to be unaffected by the annealing procedure until 650 °C, had already vanished at 850 °C. The oxidation-dehydroxylation of allanite is said to have been observed at around 700–725 °C (Bonazzi *et al.* 2009; Hoshino *et al.* 2010). Although the exact temperature for the reaction was not directly observed in this study, changes did occur between the temperatures employed.

XRD Analysis

The XRD patterns of the untreated samples and those annealed at 450, 650, and 850 °C are presented in Figure 3. Based on the diffractogram of the untreated allanite, the Bragg reflections are best matched with the allanite-(La) (RRUFF ID R070246.2), which has lattice parameters of 8.9310 Å, 5.7078 Å, 10.186 Å, and β equal to 115.15°. All four diffractograms generally exhibit crystalline properties based on the presence of high intensity, narrow reflection.

The observed differences consist of 1) shifting of certain Bragg peaks, which may be attributed to the elongation or shortening of a specific lattice parameter due to heating; 2) broadening of peaks due to non-uniform lattice distortions and dislocations as a result of interstitial impurities caused by atomic displacement due to interaction with α -particles; and 3) decreasing or increasing peak intensities, which might be attributed to preferential re-orientation or the ordering of atoms in a particular crystal plane.

Comparing the diffractogram of allanite-(La) before and after annealing at 450 °C, a peak separation is observed between Bragg angles 18° and 19°, as shown in Figure 3.

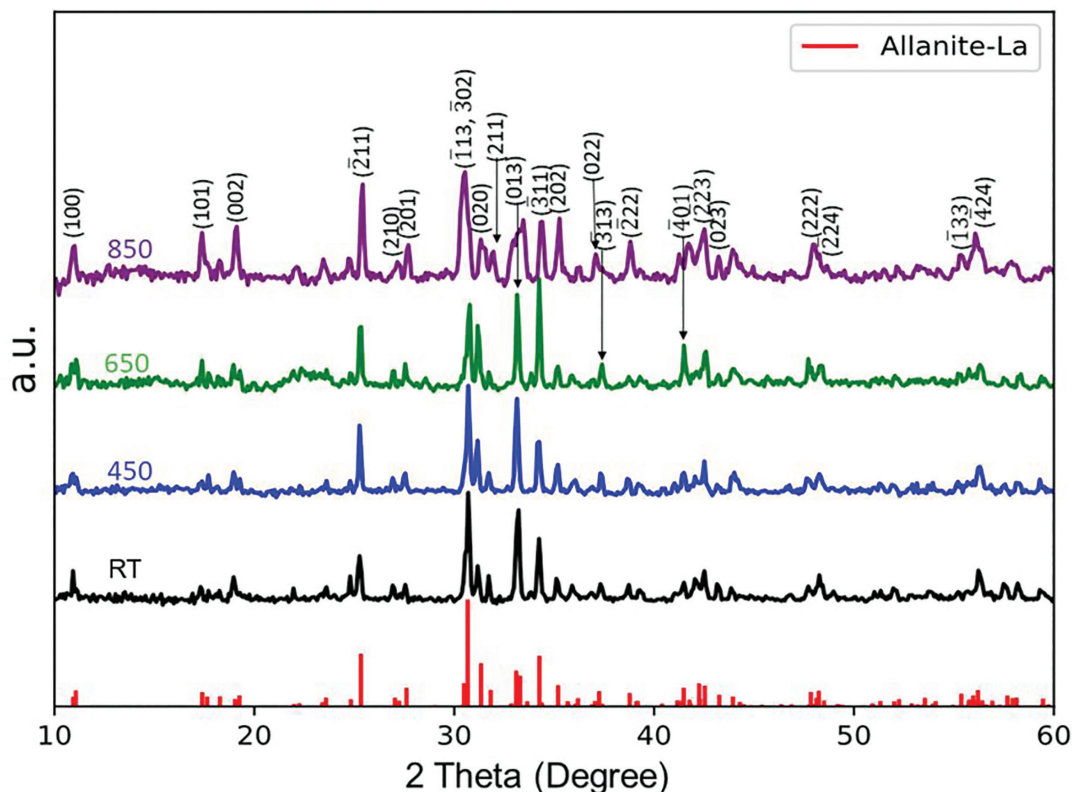


Figure 3. XRD patterns of untreated allanite and annealed at 450, 650, and 850 °C.

In the diffractogram of the untreated sample, the single peak was split upon heating, which might be attributed to (002) and the combined peak of planes (110) and ($\bar{1}11$). Annealing at 650 °C leads to further splitting into three distinct peaks, which correspond to (110), ($\bar{1}11$), and (002) planes located at $2\theta = 18.94$, 19.10 , and 19.26° , respectively. This suggests an improved alignment of dislocated atoms along these planes after heating. Annealing can lead to the recrystallization of the radiation-amorphized nanoregions and the suppression of the inherent structural defects in the crystalline fraction of the radiation-damaged sample (Gieré and Sorensen 2004; Čobić *et al.* 2010).

The changes in the Bragg peaks corresponding to planes ($\bar{2}11$), ($\bar{1}13$), (013), and ($\bar{3}11$) before and after annealing at varying temperatures are shown in Figure 4. For visualization, the positions of these planes in the crystal structure are presented in Figure 5, which are produced using Crystal Maker version 9.0. The Bragg peaks shown in Figure 4 correspond to the planes where Th, U, and REEs (Ce, La, Nd, Y, *etc.*) can be found. The peaks are more intense than others due to the high scattering factors of the heavy atoms found within these planes. These peaks were subject to analysis to evaluate the radiation damage brought by the α -decay of U and Th. The peak width can be analyzed to determine the degree of crystallinity in

terms of relative intensity and FWHM. A comparison of the FWHM is generally used as a nominal basis of crystal quality due to its sensitivity to crystal structure imperfections (Cullity and Stock 2001).

The values of the FWHM and peak intensities of the four Bragg peaks, as fitted by Gaussian curves using OriginPro version 8.0, are plotted in Figure 6 and are presented in Appendix Tables I–IV. Comparing the diffractogram of allanite-(La) before and after annealing at 450 °C, a slight decrease in the intensity and increase in FWHM of ($\bar{1}13$) plane – the most intense peak – is observed.

The decrease in the intensity of ($\bar{1}13$) peak is observed with a corresponding increase in the ($\bar{3}11$) plane. Likewise, an increase in the peak intensity of the ($\bar{2}11$) and (013) planes is also seen. This indicates the healing of defects and possible restoration of long-range order in the system that shall lead to smaller FWHM values.

From 650–850 °C, dehydroxylation is possibly causing the merging, disappearance, and broadening of peaks – particularly in the most intense ($\bar{1}13$) and (013) peaks. Increasing the temperatures or prolonging the annealing time may show degradation and amorphization behavior.

Generally, comparing the FWHM of the peaks of Bragg planes ($\bar{1}13$), (013), ($\bar{2}11$), and ($\bar{3}11$) in Figure 6b, an

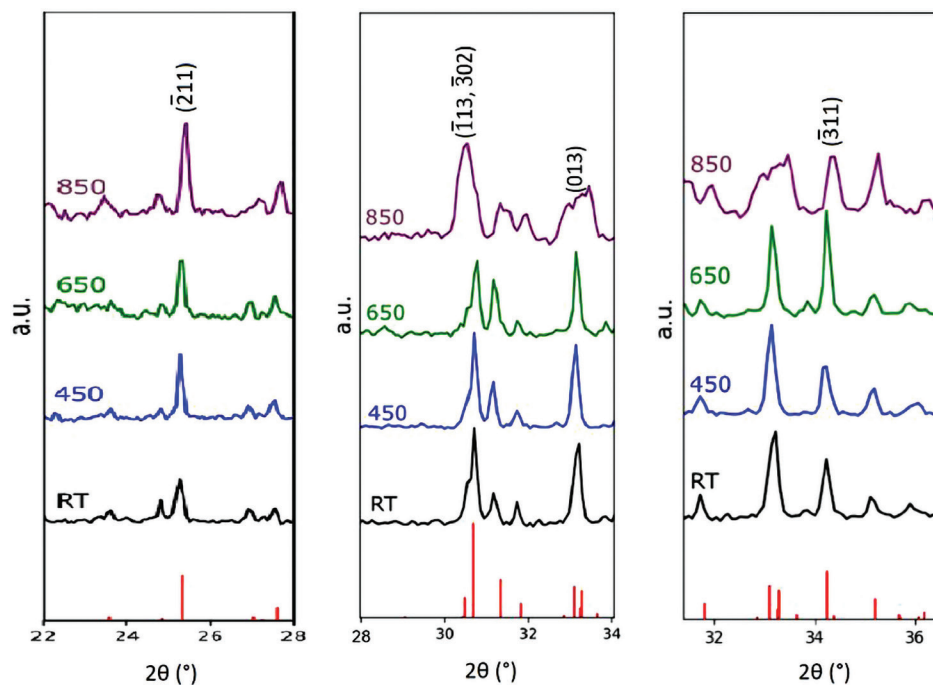


Figure 4. Changes in selected Bragg peaks with the temperature.

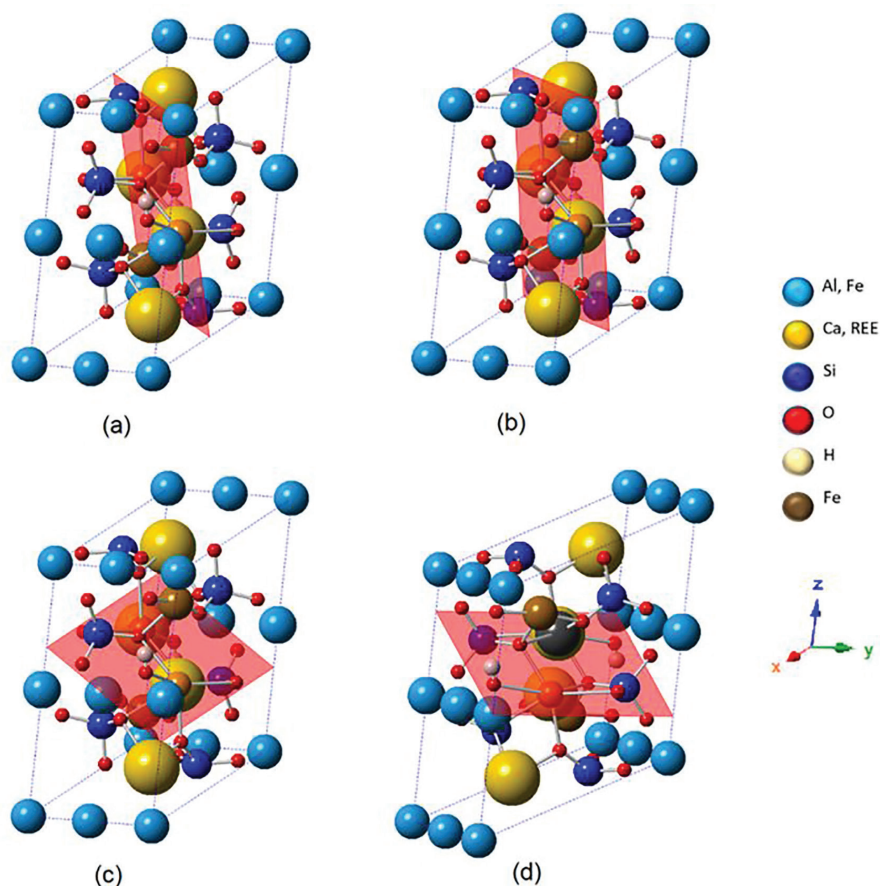


Figure 5. Bragg planes (a) (211), (b) ($\bar{3}11$), (c) (013) and (d) (113) of allanite (from Crystal Maker version 9.0).

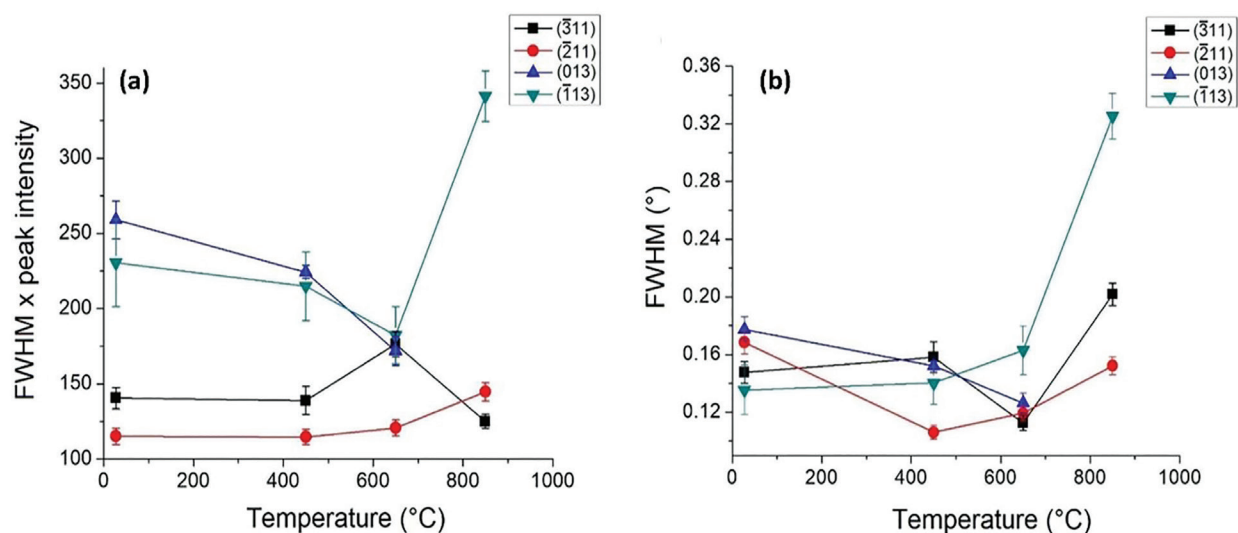


Figure 6. Correlation plot between (a) FWHM x peak intensity and annealing temperature and (b) FWHM and annealing temperature of Bragg planes $(\bar{3}11)$, $(\bar{2}11)$, (013) , and $(\bar{1}13)$.

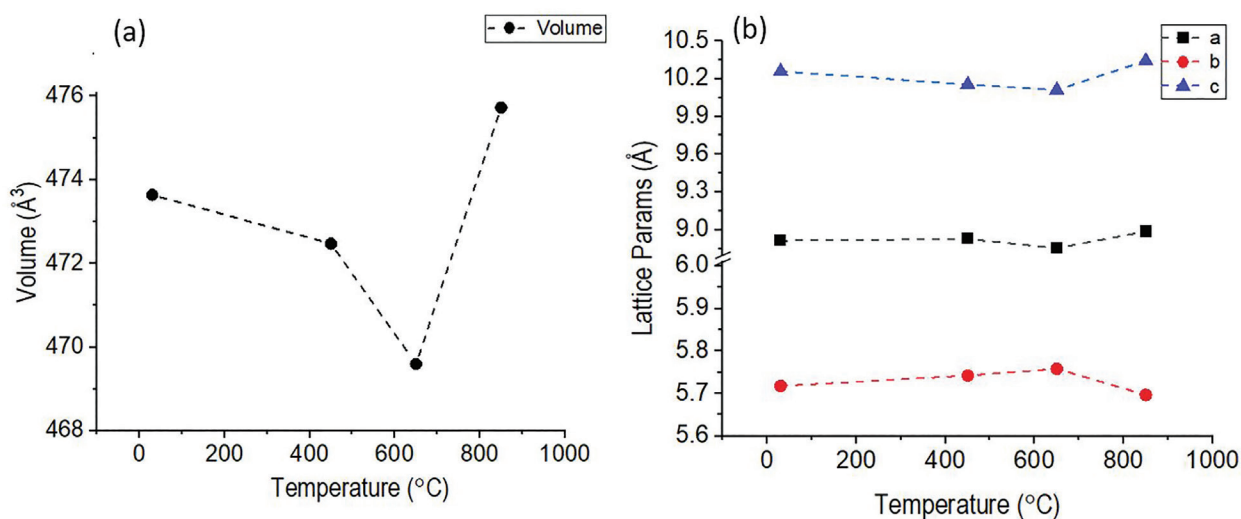


Figure 7. Correlation plots between (a) average unit cell volume and annealing temperature plus (b) lattice parameters and annealing temperature.

increase in the degree of crystallinity can be observed in the sample annealed at 450 and 650 °C, as implied by the decrease in the FWHM. This indicates the healing of defects and the reestablishment of long-range order in the system. Based on the FWHM of the (013) and $(\bar{3}11)$ Bragg reflections, the allanite-(La) annealed at 650 °C was found to have the smallest FWHM values. However, for the $(\bar{2}11)$ and $(\bar{1}13)$ peaks, the samples annealed at 450 °C show lower values.

On the other hand, all the Bragg reflections showed the largest FWHM for the sample annealed at 850 °C. In general, the recrystallization of the micro-damage occurs at a lower temperature – around 450–650 °C. Annealing

at a higher temperature, especially at 850 °C, causes significant changes to the crystal structure as the mineral slowly undergoes structure decomposition. Related studies state that the temperature at which the allanite starts to decompose is between 850–1000 °C (Janeczek and Eby 1993; Čobić *et al.* 2010); however, this is not yet evident in the results.

The evolution of the lattice parameters and the corresponding unit cell volume of the allanite-(La) with increasing annealing temperature is shown in Figure 7. The unit cell parameters are also tabulated in Table 2 and compared with the pristine allanite from Janeczek and Eby (1993). Generally, parameters *a* and *c* gradually

Table 2. Unit cell parameters of untreated and annealed allanites compared with crystalline allanite

T (°C)	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å ³)
RT	8.913 ± 0.0819	5.718 ± 0.00265	10.259 ± 0.0309	115.08 ± 1.0	473.64 ± 6.04
450	8.926 ± 0.0411	5.742 ± 0.00164	10.155 ± 0.0392	114.82 ± 0.46	472.46 ± 3.35
650	8.852 ± 0.0354	5.758 ± 0.00101	10.111 ± 0.0339	114.34 ± 0.41	469.59 ± 2.88
850	8.987 ± 0.0165	5.696 ± 0.00340	10.343 ± 0.0204	116.06 ± 0.18	475.73 ± 1.51
Ref*	8.914	5.640	10.162	115.40	461.50

*Janeczek and Eby (1993)

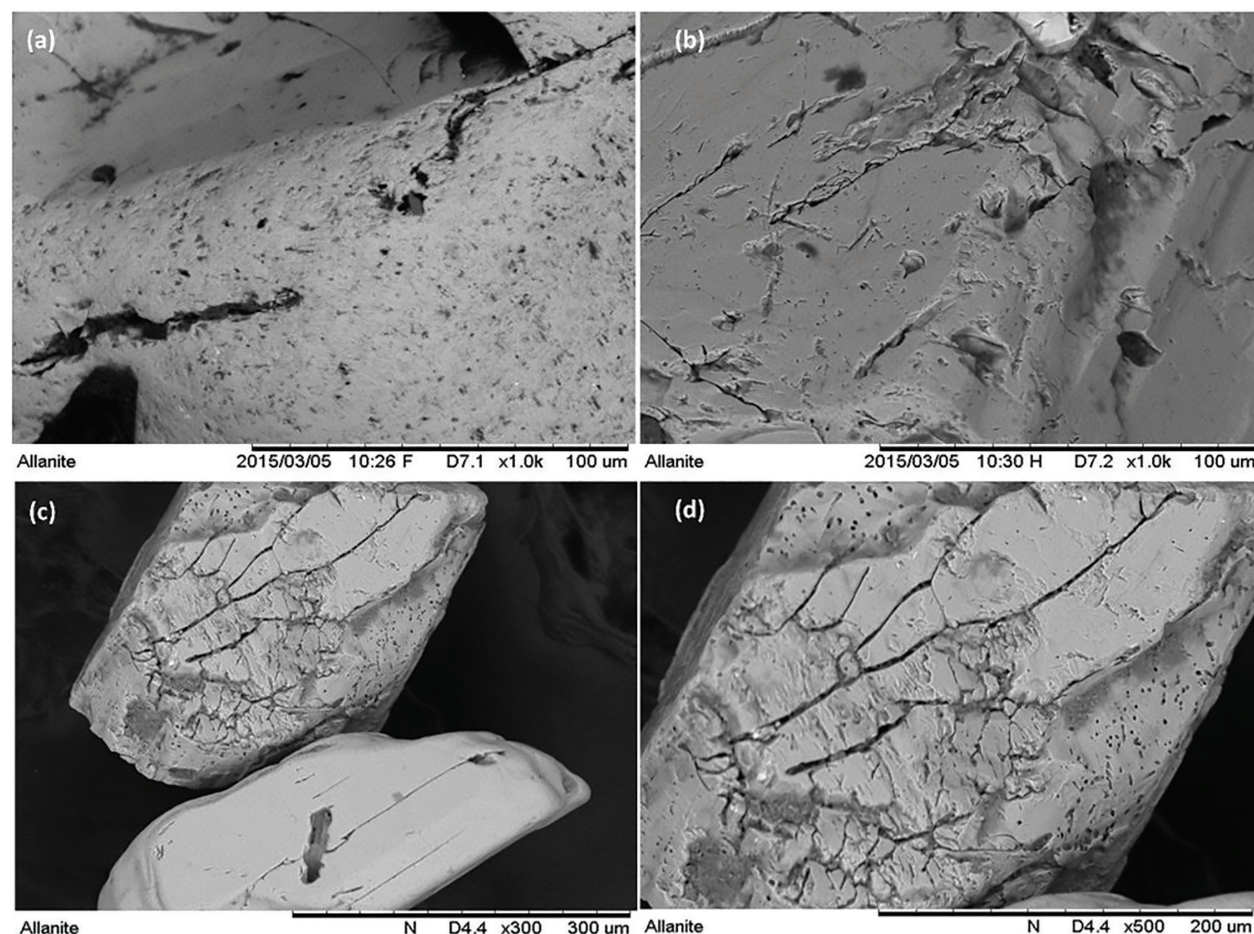


Figure 8. SEM images of allanite before annealing at (a) and (b) 1000× magnification and after heating at 850 °C at (c) 300× and (d) 500× magnification.

decrease in value at 450 and 650 °C but increase at 850 °C. Oppositely, parameter *b* increases until 650 °C but lowers in value at the highest annealing temperature. According to Bonazzi and Menchetti (1994), the *b* lattice parameter is closely correlated with the ionic radius of cations in the octahedral site and the oxidation of Fe produces a marked decrease of *b*. Likewise, the loss of OH compensating the oxidation results in the lengthening of the *c* axis.

Generally, the 1.6% decrease in the unit cell volume at 650 °C implies that the allanite-(La) becomes more crystalline as the atoms are preferentially reorganized, fixing the dislocation or displacement of atoms brought by α -decay. Recrystallization is accompanied by a decrease in the unit-cell volume, while metamictization results in a larger unit-cell volume (Janeczek and Eby 1993; Paulmann and Bismayer 2001; Čobić *et al.* 2010). However, at a higher temperature of 850 °C, the atoms

are disturbed as they acquire very high kinetic energy, which adversely affects the crystal structure as they were partially amorphized. Also, the loss of structural OH groups due to very high temperatures would not allow thermal recrystallization, as the OH groups that act as a catalyst for thermal recrystallization (Zhang *et al.* 2000) are eliminated. Comparing the unit cell volume of the annealed samples with a pristine sample in the study of Janeczek and Eby (1993), the sample annealed at 650 °C gives the nearest value with about 1.02% difference.

Surface Topography

Figure 8 shows the SEM images of allanite before and after heating at 850 °C. The untreated allanite grains show pitted regions, cavities, and cracks of varying sizes on their surface. After heating, there was an increase in the number of fractures, which are relatively longer – almost traversing the entire grain along the lengthened region. The loss of structural O-H as shown in the IR results leads to the breakdown of the structure, and the widening of FWHM Bragg peaks is proof of the degradation of the crystal structure that has caused the internal and surface cracking. Internal and surface cracking after stepwise annealing from 527–727 °C caused by heterogeneous recrystallization and hydrogen loss was also observed by Reissner *et al.* (2019).

CONCLUSION

This study investigated the structure and crystallinity of allanite-(La) from San Vicente, Palawan, Philippines, and the effects of heating on the non-metamict allanite mineral. Samples were subjected to annealing temperatures of 450, 650, and 850 °C and characterized using XRD, FTIR, and SEM analysis. The study confirmed the initial assumption of the probable existence of localized damage in the non-metamict allanite. The volume of the unit cell of the non-metamict allanite-(La) decreases after heating at 450 and 650 °C, suggesting a partial recovery of lattice defects. This indicates that the absorbed α -dose of $\sim 10^{14}$ α -decays/mg may already cause measurable changes in lattice parameters. FTIR results further confirmed the claim with the slight increase in the intensity of the Si-O band splitting upon heating, which is evident in non-metamict allanite. An onset of structure degradation was observed at 850 °C with the increase of FWHM and merging of several Bragg reflections. This can also be observed in the loss of structural O-H bonds. Moreover, this study also shows that the non-metamict allanite-(La) mineral structure responds to heating similarly to that of metamict ones reported in the literature, which undergo heterogeneous recrystallization at around 450–650 °C, as observed through cell volume contraction and increase in the intensity and/or decrease in

the FWHM of certain Bragg reflections. High-temperature annealing of metamict minerals restores their crystal structure and removes structural/lattice defects; the same effect is seen in allanite samples with localized damage.

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APPENDICES

Table I. Fitted (013) Bragg reflection positions and corresponding FWHM at varying annealing temperatures.

Annealing temp. (°C)	(013) reflection position 2θ (°)	FWHM	Peak height
Untreated	33.18	0.1775 ± 0.0087	1459.36
450	33.13	0.1521 ± 0.0029	1474.70
650	33.16	0.1263 ± 0.0070	1360.19
850	—	—	—

Table II. Fitted ($\bar{3}11$) Bragg reflection positions and corresponding FWHM at varying annealing temperatures.

Annealing temp. (°C)	($\bar{3}11$) reflection position 2θ (°)	FWHM	Peak height
Untreated	34.23	0.1477 ± 0.0075	950.56
450	34.22	0.1582 ± 0.0107	877.57
650	34.25	0.1126 ± 0.0053	1566.90
850	34.37	0.2018 ± 0.0077	619.34

Table III. Fitted ($\bar{1}13$) Bragg reflection positions and corresponding FWHM at varying annealing temperatures.

Annealing temp. (°C)	($\bar{1}13$) reflection position 2θ (°)	FWHM	Peak height
Untreated	30.69	0.1355 ± 0.0172	1700.29
450	30.69	0.1403 ± 0.0149	1531.72
650	30.72	0.1629 ± 0.0170	1119.08
850	30.78	0.3253 ± 0.0160	1049.31

Table IV. Fitted ($\bar{2}11$) Bragg reflection positions and corresponding FWHM at varying annealing temperatures.

Annealing temp. (°C)	($\bar{2}11$) reflection position 2θ (°)	FWHM	Peak height
Untreated	25.26	0.1685 ± 0.0008	683.16
450	25.28	0.1061 ± 0.0046	1080.06
650	25.30	0.1193 ± 0.0053	1011.21
850	25.39	0.1523 ± 0.0063	949.41