Vibrational spectroscopic characterization of the phosphate mineral althausite
Mg₂(PO₄)(OH,F,O) – implications for the molecular structure

Ray L. Frost⁎, Andrés López⁎, Yunfei Xi⁎, Ricardo Scholz⁎

⁎ School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG, 35,400-00, Brazil

Abstract:
Natural single-crystal specimens of althausite from Brazil, with general formula Mg₂(PO₄)(OH,F,O) were investigated by Raman and infrared spectroscopy. The mineral occurs as a secondary product in granitic pegmatites. The Raman spectrum of althausite is characterized by bands at 1020, 1033 and 1044 cm⁻¹, assigned to ν₁ symmetric stretching modes of the HOPO₃⁻ and PO₄³⁻ units. Raman bands at around 1067, 1083 and 1138 cm⁻¹ are attributed to both the HOP and PO antisymmetric stretching vibrations. The set of Raman bands observed at 575, 589 and 606 cm⁻¹ are assigned to the ν₄ out of plane bending modes of the PO₄ and H₂PO₄ units. Raman bands at 439, 461, 475 and 503 cm⁻¹ are attributed to the ν₂ PO₄ and H₂PO₄ bending modes. Strong Raman bands observed at 312, 346 cm⁻¹ with shoulder bands at 361, 381 and 398 cm⁻¹ are assigned to MgO stretching vibrations. No bands which are attributable to water were found. Vibrational spectroscopy enables aspects of the molecular structure of althausite to be assessed.

Keywords: althausite, phosphate, Raman, infrared, pegmatite

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)
P +61 7 3138 2407 F: +61 7 3138 1804
1. Introduction

Althausite $\text{Mg}_2(\text{PO}_4)(\text{OH},\text{F},\text{O})$ is a hydroxy phosphate of magnesium. The mineral is found in complex granitic pegmatites, formed by oxidation and hydration of primary minerals. The mineral originates from Minas Gerais [1], at the Sapucaia pegmatite mine, about 50 km east-southeast of Govenador Valdares, and in good crystals from the Criminoso pegmatite mine, about 35 km north. The mineral varies in colour from dark blue-green to black. The mineral is found at many sites worldwide [1-9] including at Olary, South Australia [9], and is found in magnetite-serpentinite deposits. The name of the mineral honors Professor Egon Althaus (1933– ), Karlsruhe University, Karlsruhe, Germany.

The mineral is orthorhombic [10], pseudotetragonal with point group: $2/m$. The cell data is $\text{Space Group: } P21/c$, with $a = 8.258$, $b = 6.054$, $c = 14.383$, $\beta = 120 150$ and $Z = 4$.

According to Roemming and Raade, magnesium atoms occur in both five- and six-fold coordination, and the coordination polyhedra are highly distorted [10]. The Mg octahedra form chains along D by edge-sharing. Hydroxyl and fluorine occur in a largely ordered distribution among two different structural sites and occupy alternating positions along 'channels' parallel to D. The mineral is related to the mineral wagnerite $\text{Mg}_2\text{PO}_4\text{F}$ [11-14]. Wagnerite may be considered the fluorine end-member and althausite, the hydroxyl end member. Another mineral, which is chemically closely related to althausite, is holtedahlite $\text{Mg}_2\text{PO}_4\text{OH}$ [15]. Althausite has some formal structural features in common with the minerals libethenite-olivenite-adamite-eveite-andalusite, in that they contain similar cation polyhedra with 5- and 6-coordination and the same kind of edge-sharing octahedral chains [12, 16]. Complex phase relationships exist in the $\text{MgO-P}_2\text{O}_5\text{-H}_2\text{O}$ system [11].

Raman spectroscopy has proven most useful for the study of mineral structures. The objective of this research is to report the Raman and infrared spectra of althausite and to relate the spectra to the molecular structure of the mineral. This is the first report of a systematic study of the mineral althausite from Brazil.
2. Experimental

2.1 Samples description and preparation

The althausite sample studied in this work was collected from Minas Gerais [1], at the Sapucaia pegmatite mine, about 50 km east-southeast of Governador Valadares. The sample was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-024.

2.2 Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br). Althausite crystal cleavage fragment was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment.

2.3 Raman microprobe spectroscopy

Crystals of althausite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm\(^{-1}\) and a precision of ± 1 cm\(^{-1}\) in the range between 200 and 4000 cm\(^{-1}\). Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm\(^{-1}\) line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

2.4 Infrared spectroscopy

Infrared spectra were obtained using 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 128 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.
Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package that 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 Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian 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.

3. Results and discussion

3.1 Vibrational Spectroscopy Background

In aqueous systems, the Raman spectra of phosphate oxyanions show a symmetric stretching mode ($\nu_1$) at 938 cm$^{-1}$, an antisymmetric stretching mode ($\nu_3$) at 1017 cm$^{-1}$, a symmetric bending mode ($\nu_2$) at 420 cm$^{-1}$ and a $\nu_4$ bending mode at 567 cm$^{-1}$ [17-19]. S.D. Ross in Farmer listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [20]. The vibrational spectrum of the dihydrogen phosphate anion has been reported by Farmer [20]. The PO$_2$ symmetric stretching mode occurs at 1072 cm$^{-1}$ and the POH symmetric stretching mode at $\sim$878 cm$^{-1}$. The POH antisymmetric stretching mode was found at 947 cm$^{-1}$ and the P(OH)$_2$ bending mode at 380 cm$^{-1}$. The band at 1150 cm$^{-1}$ was assigned to the PO$_2$ antisymmetric stretching mode. The position of these bands will shift according to the crystal structure of the mineral.

The vibrational spectra of phosphate minerals have been published by Farmer’s treatise Chapter 17 [20]. The Table 17.III in ref. [20] reports the band positions of a wide range of phosphates and arsenates. The band positions for the monohydrogen phosphate anion of disodium hydrogen phosphate dihydrate is given as $\nu_1$ at 820 and 866 cm$^{-1}$, $\nu_2$ at around 460 cm$^{-1}$, $\nu_3$ as 953, 993, 1055, 1070, 1120 and 1135 cm$^{-1}$, $\nu_4$ at 520, 539, 558, 575 cm$^{-1}$. The POH unit has vibrations associated with the OH specie. The stretching vibration of the POH units was tabulated as 2430 and 2870 cm$^{-1}$, and bending modes at 766 and 1256 cm$^{-1}$. Water stretching vibrations were found at 3050 and 3350 cm$^{-1}$. The position of the bands for the disodium hydrogen phosphate is very dependent on the waters of hydration. There have been
several Raman spectroscopic studies of the monosodium dihydrogen phosphate chemicals [21-25].

3.2 Vibrational Spectroscopy

The Raman spectrum of althausite over the 100 to 4000 cm\(^{-1}\) spectral range is illustrated in Figure 1a. This figure shows the peak position and the relative intensities of the Raman bands. It is noted there are large parts of the spectrum where no intensity is observed and therefore, the spectrum is subdivided into sections based upon the types of vibration being studied. The infrared spectrum of althausite over the 500 to 4000 cm\(^{-1}\) spectral range is reported in Figure 1b. This figure shows the position and relative intensities of the infrared bands. There are large parts of the infrared spectrum where little or no intensity is observed. Hence, the spectrum is subdivided into sections based on which bands are being studied.

The Raman spectrum of althausite over the 800 to 1200 cm\(^{-1}\) spectral range are reported in Figure 2a. The Raman spectrum of althausite in this spectral region shows complexity with a series of overlapping bands. The chemistry of althausite is such that it is expected to have interactions between the phosphate and hydroxyl units. This means that HOPO\(_3\)\(^3-\) units will form. Raman bands are observed at 964, 986 and 993 cm\(^{-1}\). It is proposed that these three bands are attributed to the PO stretching vibrations of HOPO\(_3\)\(^3-\), PO\(_4\)\(^3-\) and H\(_2\)PO\(_4\)\(^-\) units. According to Roemming and Raade [10], the phosphate units in the crystal structure of althausite are not equivalent and the interaction with the hydroxyl or fluorine units will be different, so it is not unexpected that a number of phosphate stretching vibrations would be observed.

Galy [23] first studied the polarized Raman spectra of the H\(_2\)PO\(_4\)\(^-\) anion. Choi et al. reported the polarization spectra of NaH\(_2\)PO\(_4\) crystals. Casciani and Condrate [26] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate (Ca(H\(_2\)PO\(_4\))\(_2\)), monocalcium dihydrogen phosphate hydrate (Ca(H\(_2\)PO\(_4\))\(_2\)·H\(_2\)O) and octacalcium phosphate (Ca\(_8\)H\(_2\)(PO\(_4\))\(_6\)·5H\(_2\)O). These authors determined band assignments for Ca(H\(_2\)PO\(_4\)) and reported bands at 1012 and 1085 cm\(^{-1}\) as POH and PO stretching vibrations, respectively. The three Raman bands at 1033, 1049 and 1062 cm\(^{-1}\) are attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [26] tabulated Raman bands at 1132 and 1155 cm\(^{-1}\) and assigned these bands to P-O symmetric and the P-O...
antisymmetric stretching vibrations. It is proposed that the proton on the hydroxyl units is very liable and can oscillate between the OH units and the phosphate units. In this way the hydrogen phosphate units are formed. The low intensity Raman bands at 968 and 988 cm\(^{-1}\) are ascribed to the hydroxyl deformation modes of the OH units in the althausite structure.

The infrared spectrum of althausite is shown in Figure 2b. This infrared spectrum shows even greater complexity than the Raman spectrum (Figure 2a). The infrared spectrum may be band component analyzed into component bands. The infrared bands at 932, 976 and 1002 cm\(^{-1}\) are assigned to the PO stretching vibrations of the HOPO\(_3\)^{3-}, PO\(_4\)^{3-} and H\(_2\)PO\(_4\) units. The three infrared bands at 1031, 1066 and 1135 cm\(^{-1}\) are assigned to the antisymmetric stretching vibrations of these units.

The Raman spectra of althausite in the 400 to 700 cm\(^{-1}\) and 100 to 400 cm\(^{-1}\) spectral range are displayed in Figure 3. The spectrum in Figure 3a may be subdivided into sections. (a) the bands at around 589 cm\(^{-1}\) (b) the bands in the 439 to 503 cm\(^{-1}\) spectral range and (c) bands in the 312 to 398 cm\(^{-1}\). In addition, there is a low intensity band at 702 cm\(^{-1}\). The Raman bands observed at 575, 589 and 606 cm\(^{-1}\) are assigned to the \(\nu_4\) out of plane bending modes of the PO\(_4\) and H\(_2\)PO\(_4\) units. The Raman spectrum of NaH\(_2\)PO\(_4\) shows bands at 526, 546 and 618 cm\(^{-1}\). The observation of multiple bands in this spectral region supports the concept of symmetry reduction of both the phosphate and hydrogen phosphate units. Raman bands at 439, 461, 475 and 503 cm\(^{-1}\) are attributed to the \(\nu_2\) PO\(_4\) and H\(_2\)PO\(_4\) bending modes. The Raman spectrum of NaH\(_2\)PO\(_4\) shows two Raman bands at 460 and 482 cm\(^{-1}\). The observation of multiple Raman bands in this spectral region for the althausite mineral supports the concept of symmetry reduction of the phosphate anion. Strong Raman bands are observed at 312, 346 cm\(^{-1}\) with shoulder bands at 361, 381 and 398 cm\(^{-1}\). These bands are assigned to MgO stretching vibrations. Again, the observation of multiple bands in this spectral region supports the concept of the non-equivalence of phosphate units in the structure of althausite. There are a number of bands in the Raman spectrum of the far low wavenumber region. These bands are ascribed to lattice vibrations.

The Raman spectrum in the 3300 to 3800 cm\(^{-1}\) spectral region is displayed in Figure 4a. The spectral profile is complex with multiple overlapping bands. Raman bands are observed at 3472, 3488, 3500, 3511 and 3523 cm\(^{-1}\). These bands are assigned to the OH stretching vibrations of the OH units in the althausite structure. From these values, a hydrogen bond
distance may be calculated of around 2.94 Å, which is in good agreement with that obtained from XRD data of 2.39 Å [10]. The Raman spectrum over the 1100 to 1400 cm\(^{-1}\) spectral range is shown in Figure 5a. No Raman bands at around 1630 cm\(^{-1}\) were observed, thus confirming the absence of water in the structure of althausite. A broad Raman peak was found at around 1320 cm\(^{-1}\) and a sharper peak at 1130 cm\(^{-1}\) was observed.

The infrared spectrum of althausite in the 2800 to 3800 cm\(^{-1}\) spectral range is reported in Figure 4b. The spectrum is broad with the main peak observed at 3500 cm\(^{-1}\). There is a long tail on the low wavenumber side and additional bands may be resolved. These bands may be attributed to the stretching vibrations of the OH units. An additional infrared band at 3679 cm\(^{-1}\) is observed. The infrared spectrum of althausite showed no bands at around 1630 cm\(^{-1}\). This indicates that no water was present (Figure 5b). Raade and Tysseland reported the infrared spectrum of althausite in their paper of 1975. They showed a stretching wavenumber for althausite at 3510 cm\(^{-1}\) [27]. These workers also synthesised the mineral analogue of althausite for which some splitting of the infrared bands occurred’ thus indicating the non-equivalence of the OH units in the structure of althausite. Such a concept is strongly supported by our Raman spectra where multiple OH stretching vibrations are observed.

4. Conclusions

Althausite is one of many phosphate minerals found in granitic pegmatites. However, this particular phosphate mineral of formula \(\text{Mg}_2(\text{PO}_4)(\text{OH,F,O})\) is an anhydrous mineral in which no water is present in the mineral formula. Whilst the colour of the mineral varies and is probably a function of the mineral origin, the mineral is often black or bluish black. Thus, it might be expected that the mineral might be difficult to measure its Raman spectrum; however this is not the case and the Raman spectra are readily obtained.

The mineral is a typical phosphate and Raman and infrared bands are attributed to HOP and PO bending and stretching vibrations of the \(\text{HOPO}_3^{3-}\) and \(\text{PO}_4^{3-}\) units. The Raman spectrum of althausite shows multiple bands attributable to the OH units. At least four bands are observed, thus indicating the non-equivalence of the OH units in the althausite structure. The infrared spectrum displays a broad band centred upon 3500 cm\(^{-1}\). Vibrational spectroscopy enables aspects of the molecular structure of althausite to be assessed.
Acknowledgments

The financial and infra-structure support of the Discipline of Nanotechnology and Molecular Science, Science and Engineering Faculty of the Queensland University of Technology, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. The authors would like to acknowledge the Center of Microscopy at the Universidade Federal de Minas Gerais (http://www.microscopia.ufmg.br) for providing the equipment and technical support for experiments involving electron microscopy. R. Scholz thanks to CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico (grant No. 306287/2012-9).
References


List of Figures

Figure 1 (a) Raman spectrum of althausite over the 100 to 4000 cm$^{-1}$ spectral range (b)
Infrared spectrum of althausite over the 500 to 4000 cm$^{-1}$ spectral range

Figure 2 (a) Raman spectrum of althausite over the 800 to 1400 cm$^{-1}$ spectral range (b)
Infrared spectrum of althausite over the 500 to 1300 cm$^{-1}$ spectral range

Figure 3 (a) Raman spectrum of althausite over the 400 to 700 cm$^{-1}$ spectral range (b)
Raman spectrum of althausite over the 100 to 400 cm$^{-1}$ spectral range

Figure 4 (a) Raman spectrum of althausite over the 3300 to 3800 cm$^{-1}$ spectral range (b)
Infrared spectrum of althausite over the 2800 to 3800 cm$^{-1}$ spectral range

Figure 5 (a) Raman spectrum of althausite (upper spectrum) in the 1100 to 1400 cm$^{-1}$ spectral range (b) infrared spectrum of althausite (lower spectrum) in the 1300 to 1700 cm$^{-1}$ spectral range
Figure 1 (a) Raman spectrum of althausite over the 100 to 4000 cm$^{-1}$ spectral range (b) Infrared spectrum of althausite over the 500 to 4000 cm$^{-1}$ spectral range
Figure 2 (a) Raman spectrum of althausite over the 800 to 1100 cm\(^{-1}\) spectral range (b) Infrared spectrum of althausite over the 800 to 1200 cm\(^{-1}\) spectral range
Figure 3a Raman spectrum of althausite (upper spectrum) in the 400 to 700 cm\(^{-1}\) spectral range and Figure 3b Raman spectrum of althausite (lower spectrum) in the 100 to 400 cm\(^{-1}\) spectral range.
Figure 4a Raman spectrum of althausite (upper spectrum) in the 1900 to 2400 cm$^{-1}$ spectral range and Figure 4b infrared spectrum of althausite (lower spectrum) in the 2800 to 3500 cm$^{-1}$ spectral range.
Figure 5a Raman spectrum of althausite (upper spectrum) in the 1100 to 1400 cm\(^{-1}\) spectral range and Figure 5b infrared spectrum of althausite (lower spectrum) in the 1300 to 1700 cm\(^{-1}\) spectral range