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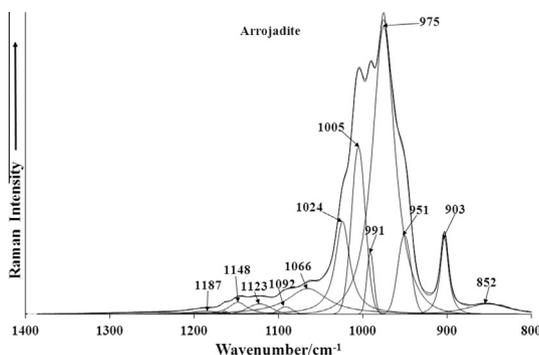
The phosphate mineral arrojadite-(KFe) and its spectroscopic characterization

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HIGHLIGHTS

- We have undertaken a study of the arrojadite-(KFe) mineral.
- Electron probe analysis shows the formula of the mineral is complex.
- The complexity of the mineral formula is reflected in the vibrational spectroscopy.
- Vibrational spectroscopy enables new information about this complex phosphate mineral arrojadite to be obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

The arrojadite-(KFe) mineral has been analyzed using a combination of scanning electron microscopy and a combination of Raman and infrared spectroscopy. The origin of the mineral is Rapid Creek sedimentary phosphatic iron formation, northern Yukon. The formula of the mineral was determined as $K_{2.06}Na_2Ca_{0.89}Na_{3.23}(Fe_{7.82}Mg_{4.40}Mn_{0.78})_{\Sigma 13.00}Al_{1.44}(PO_4)_{10.85}(PO_3OH_{0.23})(OH)_2$.

The complexity of the mineral formula is reflected in the spectroscopy. Raman bands at 975, 991 and 1005 cm^{-1} with shoulder bands at 951 and 1024 cm^{-1} are assigned to the PO_4^{3-} ν_1 symmetric stretching modes. The Raman bands at 1024, 1066, 1092, 1123, 1148 and 1187 cm^{-1} are assigned to the PO_4^{3-} ν_3 antisymmetric stretching modes. A series of Raman bands observed at 540, 548, 557, 583, 604, 615 and 638 cm^{-1} are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The ν_2 PO_4 and H_2PO_4 bending modes are observed at 403, 424, 449, 463, 479 and 513 cm^{-1} . Hydroxyl and water stretching bands are readily observed. Vibrational spectroscopy enables new information about the complex phosphate mineral arrojadite-(KFe) to be obtained.

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Introduction

The arrojadite mineral group is a complex group of phosphates with general chemical formula given as: $A_2B_2Ca_1Na_{2+x}M_{13-2x}R(PO_4)_{11}(PO_3OH_{1-x})W_2$, where the site A is occupied by large and divalent cations (Ba, Sr, Pb) plus vacancy, or monovalent cations (K, Na). The B site is occupied by either small divalent cations (Fe, Mn, Mg) plus vacancy, or monovalent cations (Na). The M site is essentially occupied by Fe^{2+} or Mn^{2+} and possibility of substitu-

tion by Mg, Zn, Li. R are trivalent cations (Al, Fe^{3+}) and W are OH^- and F^- [1]. The nomenclature of arrojadite group was established by Chopin et al. [2].

The crystal structure of arrojadite was first described by Krutik et al. [3] and later refined by Merlino et al. [4], Moore et al. [5], Steele [6] and Cámara et al. [1]. The structure of a synthetic Fe^{3+} arrojadite was refined by Yakubovich et al. [7]. Arrojadite group minerals crystallizes in the monoclinic crystal system, Space Group Cc [1]. Unit cell parameters are variable between the members of the group, however refined data for arrojadite-(KFe) are still not available and are restricted to the data published by Lindberg [8].

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Table 1

Chemical composition of arrojadite-(KFe) from the Rapid Creek, Yukon, Canada. H₂O calculated by stoichiometry.

Constituent	wt.%	Number of cations
P ₂ O ₅	46.08	11.84
Fe ₂ O ₃	25.38	7.82
Na ₂ O	9.06	5.33
MgO	7.16	4.40
Al ₂ O ₃	4.03	1.44
CaO	2.75	0.89
MnO	2.24	0.78
K ₂ O	2.20	2.06
H ₂ O	1.10	2.23
Total	100.00	36.79

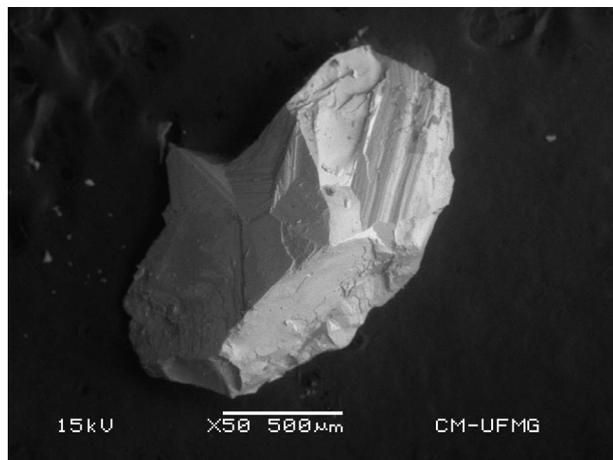


Fig. 1. Backscattered electron image (BSI) of arrojadite-(KFe) single crystal up to 2.0 mm in length.

In recent years, the application of spectroscopic techniques for the understanding the structure of phosphate minerals is increasing, with special attention to Al phosphates [9–12].

Farmer [13] divided the vibrational spectra of phosphates according to the presence, or absence of water and hydroxyl units. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm⁻¹, the antisymmetric

stretching mode (ν_3) at 1017 cm⁻¹, the symmetric bending mode (ν_2) at 420 cm⁻¹ and the ν_4 mode at 567 cm⁻¹ [14–17]. The value for the ν_1 symmetric stretching vibration of PO₄ units as determined by infrared spectroscopy was given as 930 cm⁻¹ (augelite), 940 cm⁻¹ (wavellite), 970 cm⁻¹ (rockbridgeite), 995 cm⁻¹ (dufrénite) and 965 cm⁻¹ (beraunite). The position of the symmetric stretching vibration is dependent upon the crystal chemistry of the mineral and is a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO₄ units.

The value for the ν_2 symmetric bending vibration of PO₄ units as determined by infrared spectroscopy was given as 438 cm⁻¹ (augelite), 452 cm⁻¹ (wavellite), 440 and 415 cm⁻¹ (rockbridgeite), 455, 435 and 415 cm⁻¹ (dufrénite) and 470 and 450 cm⁻¹ (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the PO₄ units. This symmetry reduction is also observed through the ν_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015 cm⁻¹ [18]; wavellite at 1145, 1102, 1062 and 1025 cm⁻¹; rockbridgeite at 1145, 1060 and 1030 cm⁻¹; dufrénite at 1135, 1070 and 1032 cm⁻¹; and beraunite at 1150, 1100, 1076 and 1035 cm⁻¹.

In this work, spectroscopic investigation of monomineral arrojadite-(KFe) sample from Rapid Creek, Yukon, Canada has been carried out. The analysis includes spectroscopic characterization of the structure with infrared and Raman spectroscopy. Chemical analysis was applied to support the mineral characterization.

Experimental

Samples description and preparation

The arrojadite-(KFe) sample forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB065. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The arrojadite-(KFe) sample was phase analyzed by X-ray diffraction.

The Rapid Creek sedimentary phosphatic iron formation comprises the upper and youngest portion of an Aptian–Albian flyschoid sequence which reaches a maximum thickness of 4 km

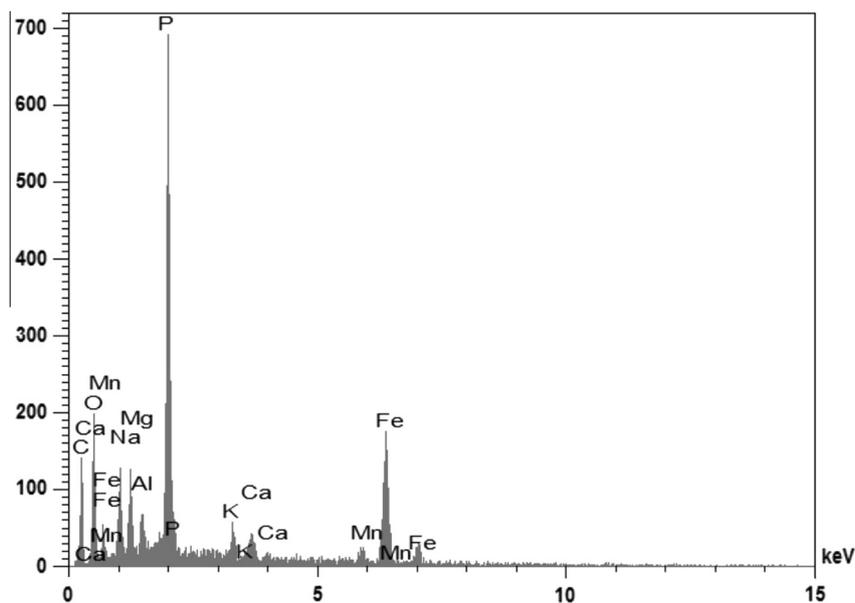


Fig. 2. EDS spectra of arrojadite-(KFe).

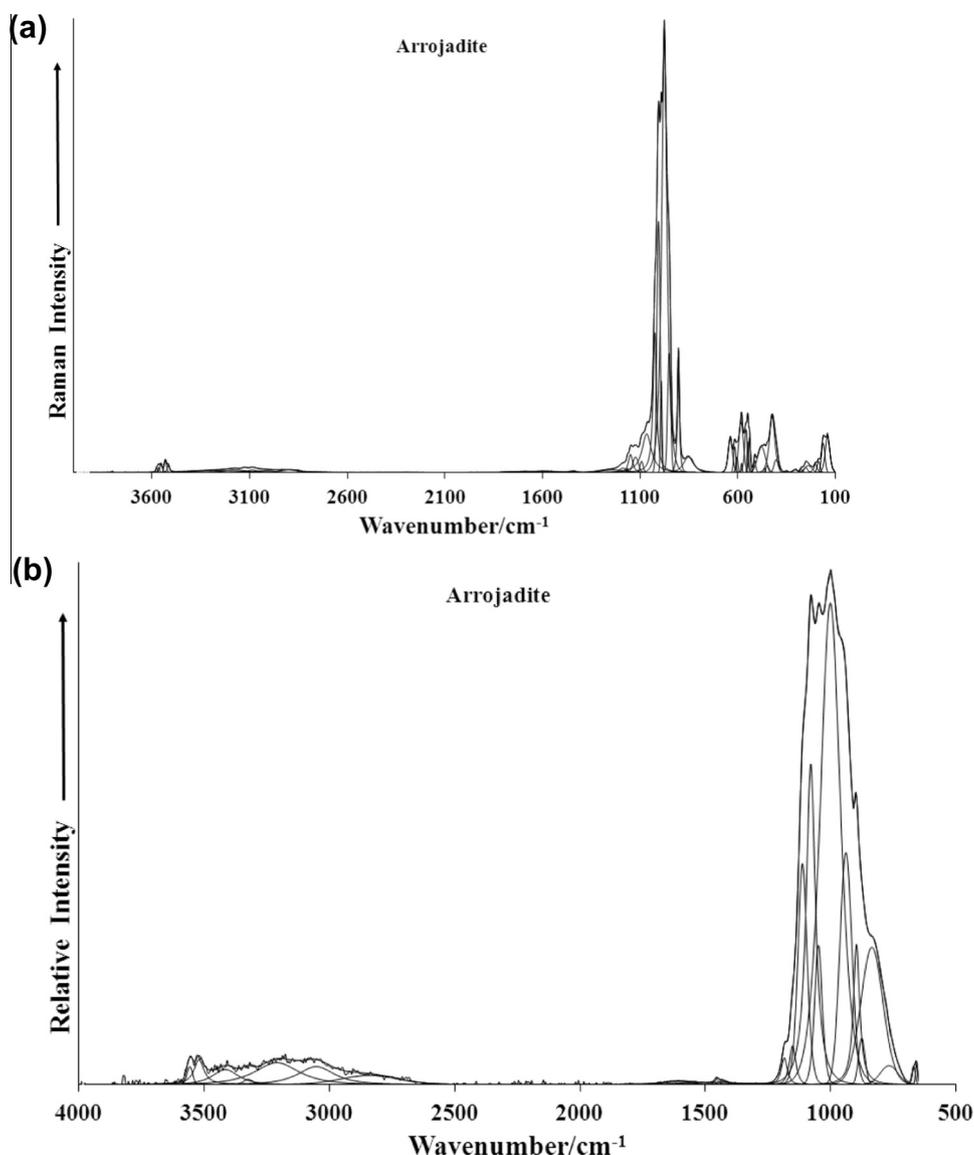


Fig. 3. (a) Raman spectrum of arrojadite-(KFe) over the 100–3600 cm^{-1} spectral range (b) infrared spectrum of arrojadite-(KFe) over the 500–4000 cm^{-1} spectral range.

in the Blow Trough. The phosphate association is composed mainly of rare minerals such as satterlyite, arrojadite group minerals, augelite, lazulite and gormanite, which reflect an original calcium-deficient composition. The deposition of iron and magnesium phosphates as well as apatite is strongly indicated, and this condition is unique for marine phosphorites [19].

Scanning electron microscopy (SEM)

Arrojadite-(KFe) crystals were coated with a 5 nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

Raman microprobe spectroscopy

Crystals of arrojadite-(KFe) were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10 \times , 20 \times , and 50 \times objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also in-

cludes 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 $\pm 1 \text{ cm}^{-1}$ in the range between 200 and 4000 cm^{-1} . Repeated acquisitions on the crystals using the highest magnification (50 \times) 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.

An image of the arrojadite-(KFe) crystals measured is shown in the supplementary information as Fig. S1. Clearly the crystals of arrojadite-(KFe) are readily observed, making the Raman spectroscopic measurements readily obtainable.

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.

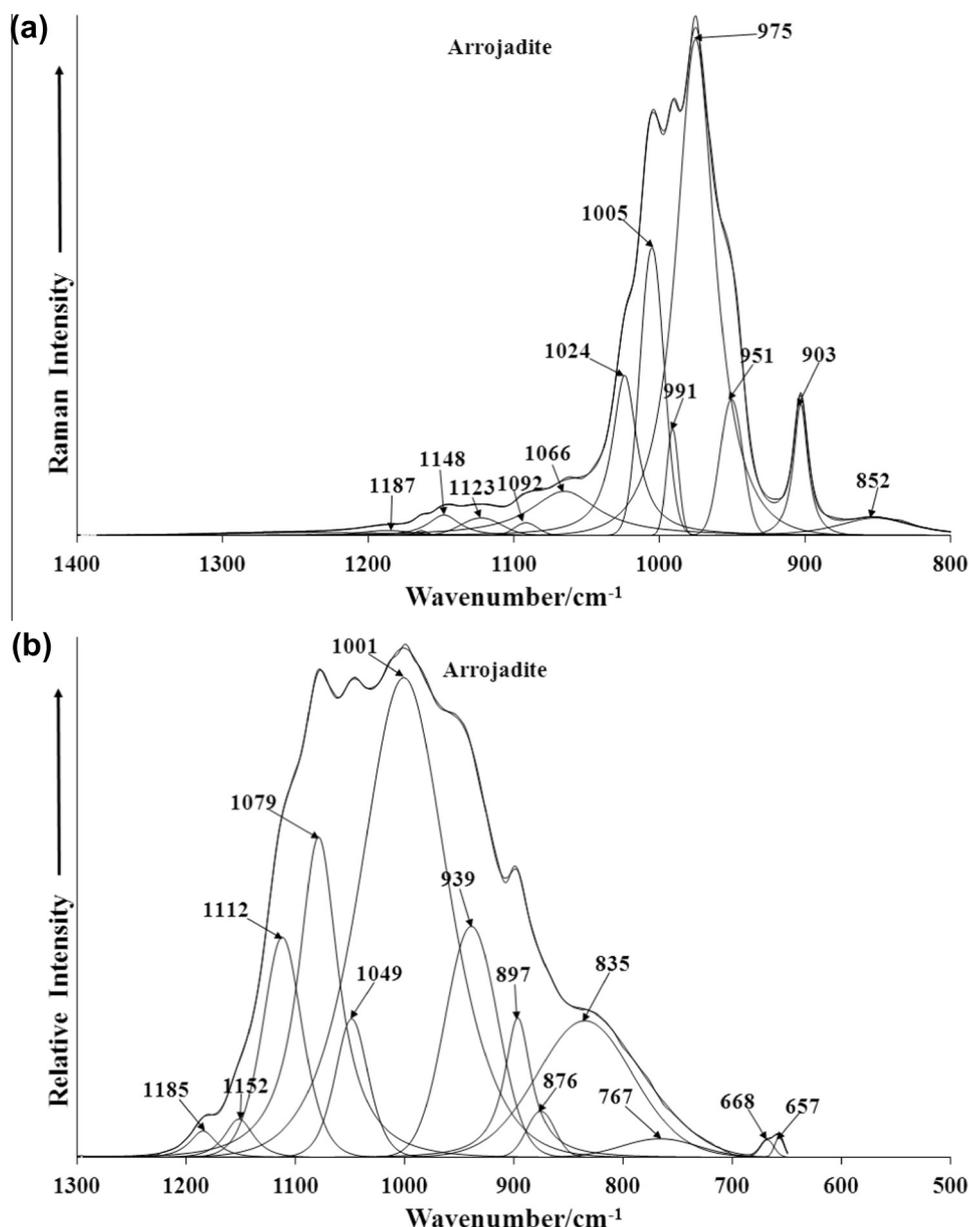


Fig. 4. (a) Raman spectrum of arrojadite-(KFe) (upper spectrum) in the 800–1400 cm⁻¹ spectral range and (b) Infrared spectrum of arrojadite-(KFe) (lower spectrum) in the 500–1300 cm⁻¹ spectral range.

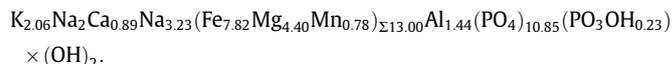
Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function 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.

Results and discussion

Chemical characterization

The back scattered electron image (BSI) of arrojadite-(KFe) sample studied in this work is shown in Fig. 1. The fragment

shows homogeneous composition. Qualitative and semi-quantitative chemical composition shows a complex Fe, K, Na, Mg and Al phosphate and with minor amounts of Ca and Mn. Fluorine was not observed and the mineral is considered as OH end member. The semi-quantitative chemical data were recalculated considering 1.10% of H₂O in the structure, as expected for the arrojadite-(KFe) end member. The M site was recalculated on the basis of 13 cations. According to the crystal structure, 100% of Fe was considered as Fe²⁺. The EDS spectra of arrojadite-(KFe) and its chemical analysis is shown in Fig. 2. The chemical formula was calculated on the basis of 50 O atoms (O, OH) and can be expressed as:



The results indicate an arrojadite-(KFe) mineral. The chemical analysis is given in Table 1.

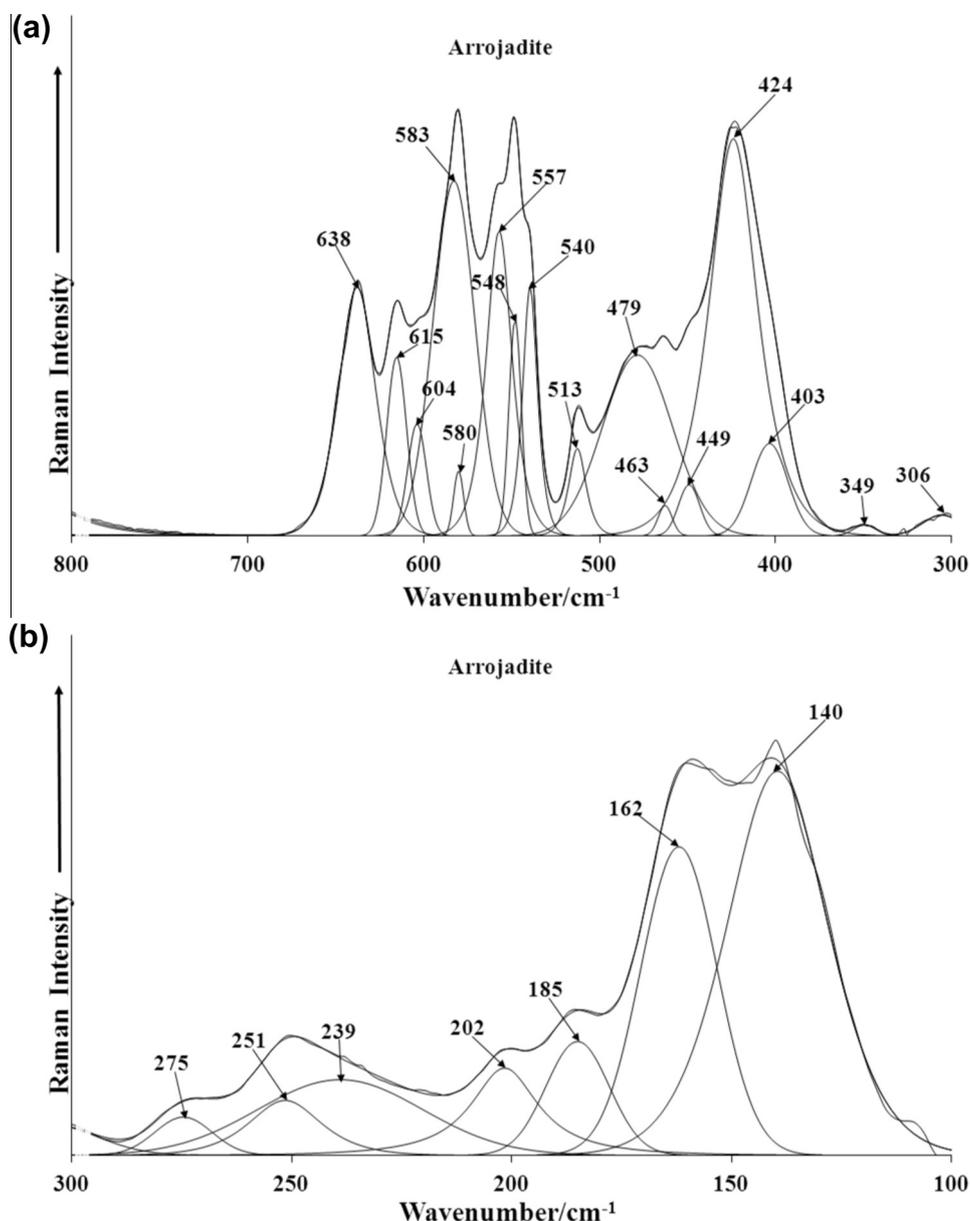


Fig. 5. (a) Raman spectrum of arrojadite-(KFe) (upper spectrum) in the 300–800 cm^{-1} spectral range and (b) Raman spectrum of arrojadite-(KFe) (lower spectrum) in the 100–300 cm^{-1} spectral range.

Spectroscopy

One most beneficial way of studying phosphate minerals is to undertake vibrational spectroscopy. In this way, the symmetry and distortion of the phosphate units in the mineral structure can be ascertained. Further, if there are different sometimes called non-equivalent phosphate units, then vibrational spectroscopy can determine if the phosphate units are identical or different. The Raman spectrum of arrojadite-(KFe) over the 100 to 3600 cm^{-1} spectral region is displayed in Fig. 3a. This figure shows the position and relative intensity of the Raman bands. It is obvious that the less intense spectral region is over the 2600–4000 cm^{-1} region. This region is where the water and OH stretching vibrations are likely to be observed. The overall spectrum may be subdivided into sections depending upon the type of vibration being studied. The infrared spectrum over the 500–4000 cm^{-1} spectral range is shown in Fig. 3b.

The Raman spectrum of arrojadite-(KFe) in the 800 to 1400 cm^{-1} spectral range is reported in Fig. 4a. The Raman spec-

trum shows complexity with a number of overlapping bands. Intense Raman bands are observed at 975, 991 and 1005 cm^{-1} with shoulder bands at 951 and 1024 cm^{-1} . These bands are assigned to the PO_4^{3-} ν_1 symmetric stretching modes. Multiple bands are observed depending upon to which cation the phosphate is bonding. Raman bands are observed at 1024, 1066, 1092, 1123, 1148 and 1187 cm^{-1} and are assigned to the PO_4^{3-} ν_3 antisymmetric stretching modes. The Raman band at 975 cm^{-1} is attributed to the stretching vibrations of HOPO_3^{2-} units. The broad Raman band at 852 cm^{-1} is ascribed to water librational modes. Galy [20] first studied the polarized Raman spectra of the H_2PO_4^- anion. Choi et al. reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [21] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), monocalcium dihydrogen phosphate hydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) and octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$). These authors determined band assignments for $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and reported bands at 1002 and 1011 cm^{-1} as POH and PO stretching vibrations, respectively. The two Raman bands at 1086 and 1167 cm^{-1} are

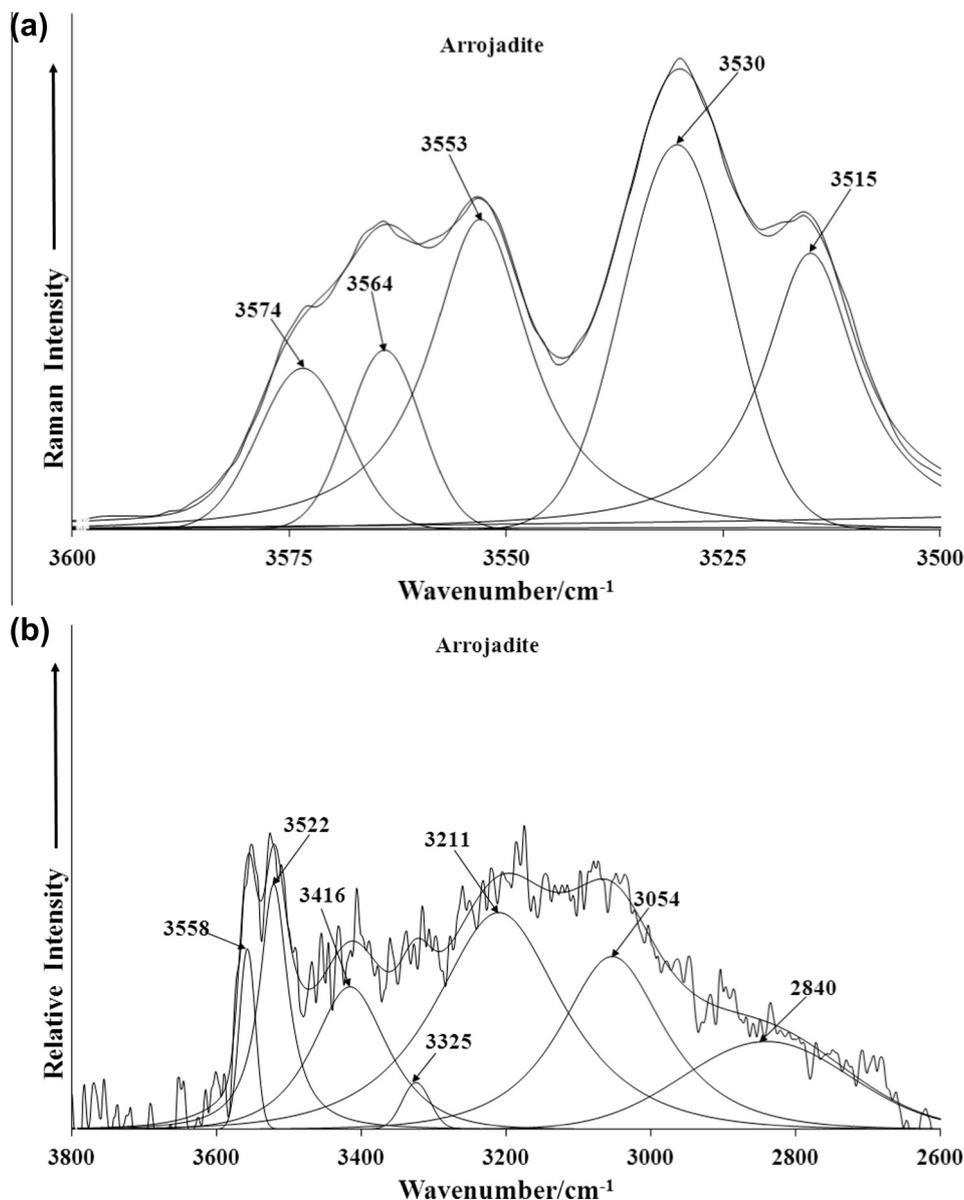


Fig. 6. (a) Raman spectrum of arrojadite-(KFe) (upper spectrum) in the 800–1400 cm^{-1} spectral range and (b) infrared spectrum of arrojadite-(KFe) (lower spectrum) in the 500–1300 cm^{-1} spectral range.

attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [21] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P–O symmetric and the P–O antisymmetric stretching vibrations. The infrared spectrum displays greater complexity with multiple overlapping bands. The complexity of the spectrum makes it difficult to undertake band assignments.

The infrared spectrum of arrojadite-(KFe) in the 500 to 1300 cm^{-1} spectral region is displayed in Fig. 4b. The infrared spectrum displays greater complexity with multiple overlapping bands. The complexity of the spectrum makes it difficult to undertake band assignments. The infrared band at 1001 cm^{-1} is assigned to the PO_4^{3-} ν_1 symmetric stretching vibration. The infrared bands at 1049, 1079, 1152 and 1185 are attributed to the PO_4^{3-} ν_3 antisymmetric stretching vibrational mode. The infrared band at 835 cm^{-1} is ascribed to water librational modes. This complexity of both the Raman and infrared spectra may be due to a mixture of different phosphate anions, namely PO_3^{3-} , HOPO_3^{2-} and $\text{H}_2\text{O}_2\text{PO}^-$. There is a difference between taking a Raman spectrum and an infrared spec-

trum. The sample spot size of the Raman spectrometer is around 1 micron. In infrared spectroscopy the measurement size is at best 30 microns. Thus in Raman spectroscopy it is possible to collect data for a pure mineral because that crystal was selected. It is more likely that the infrared spectrum is more likely to collect data for a mixture. This is why of course it is an advantage to run the Raman spectrum.

The Raman spectra of arrojadite-(KFe) in the 300 to 800 cm^{-1} and in the 100–300 cm^{-1} are displayed in Fig. 5a and b. The first spectral region is the region of the phosphate bending modes. This spectral region is where the PO_4^{3-} and HOPO_3^{2-} bending vibrations are found. A series of bands are observed at 540, 548, 557, 583, 604, 615 and 638 cm^{-1} . These bands are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The Raman spectrum of crystalline NaH_2PO_4 shows Raman bands at 526, 546 and 618 cm^{-1} (this work). A series of bands are observed at 403, 424, 449, 463, 479 and 513 cm^{-1} . These bands are attributed to the ν_2 PO_4 and H_2PO_4 bending modes. The Raman spectrum in the far wavenumber region is shown in Fig. 5b. Quite intense bands

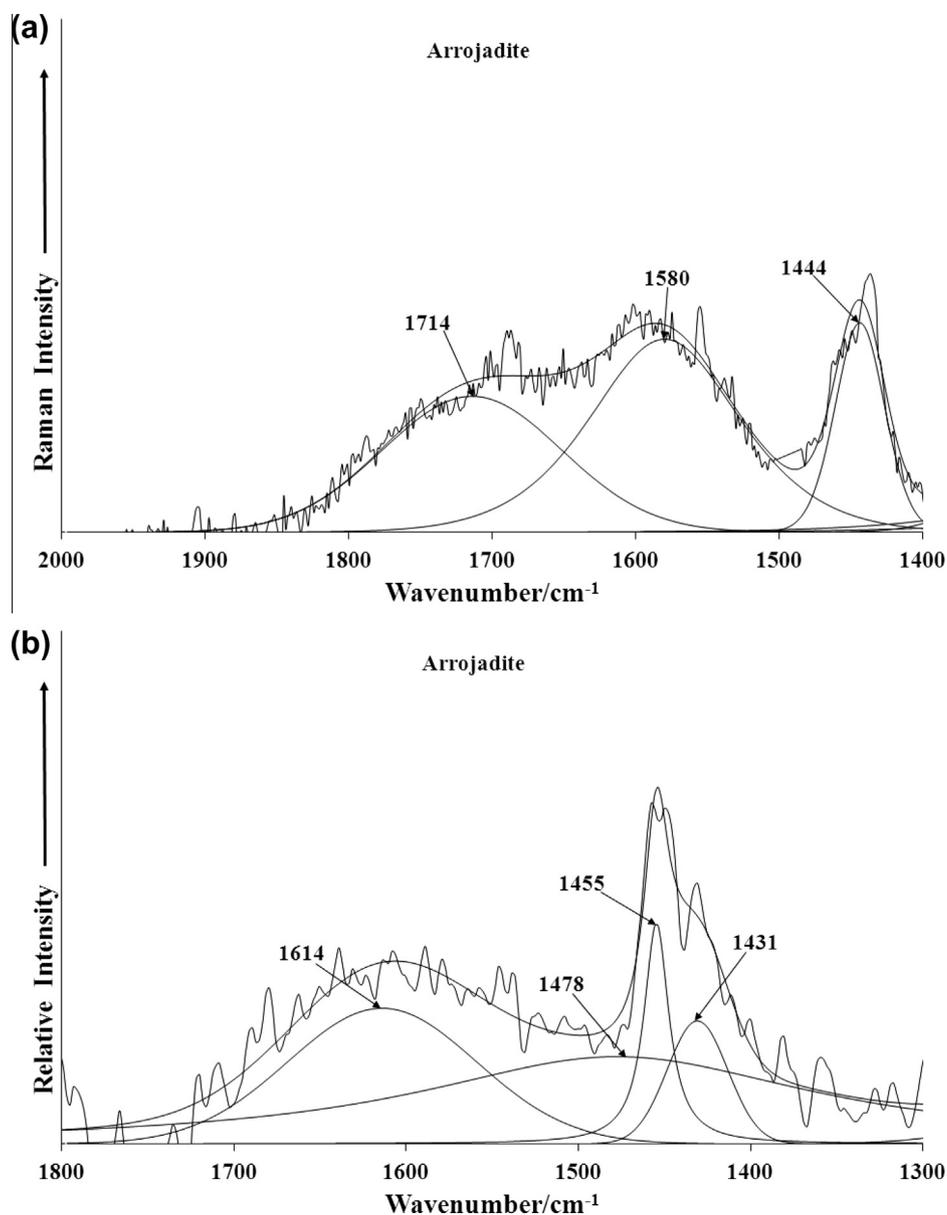


Fig. 7. (a) Raman spectrum of arrojadite-(KFe) (upper spectrum) in the 1400–2000 cm^{-1} spectral range and (b) infrared spectrum of arrojadite-(KFe) (lower spectrum) in the 1300–1800 cm^{-1} spectral range.

are found at 140, 162, 185, 202, 239, 251 and 275 cm^{-1} . These bands may be simply described as lattice vibrations.

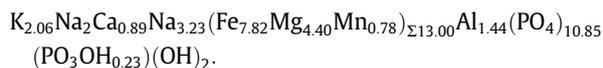
The Raman spectrum of the OH stretching region of arrojadite-(KFe) is reported in Fig. 6a and b. The first figure shows the OH stretching bands and the second the water stretching bands. Raman bands are observed at 3515, 3560, 3553, 3564 and 3574 cm^{-1} .

A comparison may be made with the infrared spectrum (Fig. 6b) where broad bands are observed at 2898, 3022, 3085, 3125, 3171 and 3268 cm^{-1} , assigned to water stretching vibrational modes. It is noted that much greater intensity of the water bands is observed in the infrared spectrum as compared with the Raman spectrum. The reason for this is that water is a very poor Raman scatterer whereas water is a very strong infrared absorber. The Raman spectrum of arrojadite-(KFe) in the 1400 to 1800 cm^{-1} and the infrared spectrum in the 1300 to 1800 cm^{-1} are shown in Fig. 7a and b. This spectral region is where the water bending modes are observed. The Raman spectrum shows a reasonably strong band at 1631 cm^{-1} assigned to the water bending mode. A similar

intense band at 1632 cm^{-1} is observed in the infrared spectrum. Other infrared bands are found at 1426 and 1575 cm^{-1} .

Conclusions

We have characterized the mineral arrojadite-(KFe) using vibrational spectroscopic techniques with support of SEM/EDS chemical analysis. The chemical formula was calculated on the basis of 50 O atoms (O, OH) and can be expressed as:



The results indicate an arrojadite-(KFe) mineral.

The mineral is characterized by an intense sharp Raman bands at 1009 cm^{-1} with shoulders at 975, 991 and 1005 cm^{-1} are assigned to stretching vibrations of PO_4^{3-} and HPO_4^{2-} units. Raman band at 991 cm^{-1} is assigned to the ν_1 symmetric stretching mode

of the POH units, whereas the Raman band at 1005 cm^{-1} is assigned to the $\nu_1\text{ PO}_4^{3-}$ symmetric stretching mode. Raman bands observed at 540, 548, 557, 583, 604, 615 and 638 cm^{-1} are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units.

The Raman bands at 3515, 3560, 3553, 3564 and 3574 cm^{-1} are assigned to water and hydroxyl stretching vibration. A comparison may be made with the infrared spectrum where broad bands are observed at 2898, 3022, 3085, 3125, 3171 and 3268 cm^{-1} , assigned to water stretching vibrational modes. The observation of multiple bands gives credence to the non-equivalence of the water units in the arrojadite-(KFe) structure.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2013.02.027>.

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