INTRODUCTION

Väyrynenite is a rare beryllium and manganese hydroxy phosphate mineral of formula MnBe(PO$_4$)(OH,F) [1, 2]. Beryllium phosphates are relatively rare in nature and are related to a range of temperature and pressures during the pegmatite evolution. Beryllium phosphates crystallize since the magmatic process as described by Rickers et al. [3] and Thomas et al., [4] to the hydrothermal and supergene [5, 6]. The most common Be phosphates in granitic pegmatites are herderite-hydroxylherderite, beryllonite and the members of the roscherite group [7, 8].

Väyrynenite is found as an alteration product of beryl and triphylite in complex zoned granite pegmatites [9, 10]. Despites the type locality in Viitaniemi pegmatite in Filand, other occurrences were reported in Paprok pegmatites in Afghanistan [11], Xiyuantou pegmatite in China [12], pegmatites of Chitral region in Pakistan [13] and Fregeneda pegmatite in Spain [14]. Väyrynenite is a rare gemstone and also shows importance in the mineral collectors market [15].

Väyrynenite is a monoclinic mineral [1, 16] with $a = 5.4044(6)$, $b = 14.5145(12)$, $c = 4.7052(6)$ Å, $\beta = 102.798(9)^\circ$, space group $P2_1/a$ and $Z = 4$. The structure of väyrynenite was determined by Mrose and Appleman [1, 16], and refined by Huminicki and Hawthorne [1, 16]. Crystal structure of väyrynenite consist of zigzag chains with composition $[\text{Be}_2(\text{OH})_2(\text{PO}_4)_2]_n^{-4n}$ cross-linked by Mn atoms between the chains and by hydrogen bonds [1, 16]. Mn atoms lie between the chains and are octahedrally coordinated by two oxygen atoms and one hydroxyl oxygen from one chain and by one
oxygen atom from each of three adjacent chains [1, 16]. Within \([\text{Be}_2(\text{OH})_2(\text{PO}_4)_2]_{n-4n}\) chain each Be atom is tetrahedrally coordinated by two oxygen atoms and by two hydroxyl oxygens; each P atom is tetrahedrally coordinated by four oxygen atoms [1, 16]. \((\text{Be}_4\varphi_4)\) tetrahedra connect to adjacent \((\text{Be}_4\varphi_4)\) tetrahedra by corner-sharing of anions in a zigzag pattern to form a chain that extends in the \(a\) direction [16]. This chain is decorated along its periphery by \((\text{PO}_4)\) tetrahedra that corner-share with one O atom from each of two different \((\text{Be}_4\varphi_4)\) tetrahedra to form ribbons along the \(a\) axis [16].

Raman spectroscopy has proven most useful for the study of mineral structure. Raman spectroscopy is an important tool in the characterization of phosphates in pegmatite rocks [17]. In recent years, spectroscopic studies of phosphate minerals are increasing, especially due to their industrial and technological importance. Published data of väyrynenite are restricted to the RRUFF Project database (http://rruff.info/vayrynenite/display=default/R050243) and also the gemological and photoluminescence library (http://www.gemmoraman.com/Libraries.aspx?id=258).

It is noted that no band assignments or explanation of the spectra are provided. Further, the spectra of the hydroxyl stretching region is not provided. The Raman spectra of väyrynenite from the RRUFF data base are given in the supplementary information. Two Väyrynenite samples are analysed: one from Finland and one from Pakistan. The first spectrum is very different from the second spectrum. In fact, the Raman spectrum of väyrynenite from Finland does not even look like a phosphate spectrum.
In this work, a sample of a väyrynenite mineral from the Viitaniemi pegmatite, Finland was selected for analysis. Studies include chemistry via scanning electron microscope with Energy-dispersive spectroscopy (SEM/EDS) and electron microprobe in the WDS mode (wavelength-dispersive spectroscopy), spectroscopic characterization of the structure with infrared and Raman spectroscopy.

METHODS

Sample Description And Preparation

The väyrynenite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-103. The studied sample is from the Viitaniemi pegmatite, located in the Eräjärvi area, Finland. The pegmatite is lithium bearing and is classified as complex type, amblygonite subtype [18, 19]. Detailed description of the pegmatite has been published [20].

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The väyrynenite studied in this work occurs in association with siderite. Scanning electron microscopy (SEM) in the EDS mode was applied to support the mineral characterization.

Chemical Characterization

Väyrynenite was characterized by Scanning electron microscopy (SEM) and electron microprobe (EMP). 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). The mineral was 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.

A quantitative chemical analysis was carried via electron microprobe (EMP). Väyrynenite fragment selected for this study was analyzed with the performance of nine spots. The chemical analysis was carried out with a Jeol JXA8900R spectrometer from the Physics Department of the Federal University of Minas Gerais, Belo Horizonte. For each selected element, we used the following standards: Fe – Magnetite, Mn – Rodhonite, F – Fluorite, P and Ca – Ca$_2$P$_2$O$_7$, Na – Albite, Sr – Celestite, Al – Al$_2$O$_3$ and Mg – MgO, Ba – Barite, Cu – Cuprite, Pb – Cerussite, As – Arsenopyrite and Zr - Zircon. The epoxy embedded väyrynenite sample was polished in the sequence of 9 µm, 6 µm and 1 µm diamond paste MetaDI® II Diamond Paste – Buhler, using water as a lubricant, with a semi-automatic MiniMet® 1000 Grinder-Polisher – Buehler. Finally, the epoxy embedded väyrynenite was coated with a thin layer of evaporated carbon. The electron probe microanalysis in the WDS (wavelength dispersive spectrometer) mode was obtained at 15 kV accelerating voltage and beam current of 10 nA. Chemical formula was calculated on the basis of five oxygen atoms (considering O and F).

**Raman Microprobe Spectroscopy**
Crystals of väyrynenite 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 polarised 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.

**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. The infrared spectra are given in the supplementary information.

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.

RESULTS AND DISCUSSION

Chemical Characterization

The SEM image of the väyrynenite single crystal studied in this work is shown in Figure 1. The crystal shows tabular habitus. Qualitative chemical analysis of väyrynenite shows a Mn phosphate with minor amounts of Ca and was applied to support the selection of elements for EMP (Figure 2). Si and Al are also observed due to microcrystals of clay in the surface. The crystal doesn’t show chemical zonation and can be considered a single mineral phase and a type material.

The quantitative chemical analysis of väyrynenite is presented in Table 1. The composition was calculated as mean values in five spots. The range of the chemical analysis is also presented and shows no significant variance. H$_2$O and BeO content were calculated by stoichiometry considering F + OH = 1. The chemical formula was calculated on the basis of 5 oxygen atoms in the structure. The chemical composition indicates a manganese phosphate with partial substitution of manganese by iron and minor magnesium. For the other analyzed elements, the measured amount is no
significant. The chemical formula of the studied sample can be expressed as:

\[(\text{Mn}^{0.88,\text{Fe}^{0.08,\text{Mg}^{0.01}})^{\text{Be}^{1.02}}(\text{PO}_4)^{1.00}(\text{OH})^{1.02}}\]

**VIBRATIONAL SPECTROSCOPY**

The Raman spectrum of väyrynenite in the 100 to 4000 cm\(^{-1}\) spectral range is shown in Figure 3a. This spectrum shows the peak position and the relative intensities in the Raman spectrum of väyrynenite. It is noted that there are large parts of the spectrum where no intensity is found. Therefore, the spectrum is subdivided into sections depending upon the type of vibration being studied. The infrared spectrum of väyrynenite in the 500 to 4000 cm\(^{-1}\) spectral range is reported in Figure 3b. This spectrum shows the peak position and the relative intensities of the infrared bands. The spectrum is subdivided into sections depending upon the type of vibration being examined.

The Raman spectrum of väyrynenite in the 800 to 1300 cm\(^{-1}\) spectral range is illustrated in Figure 4a. The Raman spectrum is dominated by an intense band at 1004 cm\(^{-1}\) with shoulders at 1009 cm\(^{-1}\) and 986 cm\(^{-1}\). These bands are assigned to the PO\(_4^{3-}\) \(\nu_1\) symmetric stretching mode. The observation of multiple bands offers support for the concept of different phosphate units in the väyrynenite structure. Not all the phosphate units are equivalent. This concept is also supported by the number of bands which are attributed to the PO\(_4^{3-}\) \(\nu_3\) antisymmetric stretching modes. Raman bands of this vibrational mode are found at 1044, 1074, 1126, 1139 and 1186 cm\(^{-1}\). A comparison may be made with the Raman spectrum for the mineral sample from Pakistan. An intense Raman band is found at 988 cm\(^{-1}\) with shoulders on both the high and low wavenumber side of the main
peak. Bands between 1050 and 1200 cm\(^{-1}\) were not observed in the RRUFF spectrum. The mineral sample from Finland shows an intense Raman band at around 1005 cm\(^{-1}\). Shoulders are also observed on either side of the main peak. It is proposed that the variation in the spectra are a function of the chemical composition of the väyrynenite sample which will be origin dependent.

A comparison may be made with spectra of other iron containing phosphate minerals such as augelite [21] and turquoise [22]. In the Raman spectrum of augelite, an intense band is observed at 1108 cm\(^{-1}\). The band is very sharp with a band widths of 7.0. This band is assigned to the \(\nu_1\) symmetric stretching mode. Breitinger et al. assigned a band at 1108 cm\(^{-1}\) for synthetic augelites to this mode. The position is in sharp contrast to the value of 930 cm\(^{-1}\) published by Farmer [23]. In the infrared spectrum the band at 1070 cm\(^{-1}\) is assigned to this mode. In the infrared spectrum bands of augelite are observed at 1204, 1171, 1142, 1102, 1070 and 1016 cm\(^{-1}\). The position of these bands may be compared with those reported by Farmer. Bands were given as 1205, 1155, 1079 and 1015 cm\(^{-1}\). The three higher wavenumber bands (1204, 1171, 1142 cm\(^{-1}\)) are attributed to the \(\nu_3\) antisymmetric PO\(_4\)\(^{3-}\) stretching vibrations. An intense band is observed at 1160 with a resolved component band at 1136 cm\(^{-1}\) which may be attributed to these vibrational modes.

The infrared spectrum in the 500 to 1300 cm\(^{-1}\) is reported in Figure 4b. The infrared spectrum shows complexity with a number of bands being resolved. The infrared bands at 1028, 1051, 1078, 1097, 1139 and 1176 cm\(^{-1}\) are assigned to the PO\(_4\)\(^{3-}\) \(\nu_3\) antisymmetric
stretching mode. The infrared band at 1004 cm\(^{-1}\) is probably due to the PO\(_4^{3-}\) \(\nu_1\) symmetric stretching mode. A very low intensity Raman band at 898 cm\(^{-1}\) is observed. This band is also observed in the infrared spectrum at 899 cm\(^{-1}\). A second infrared band is found at 921 cm\(^{-1}\). One possibility is that these bands are assignable to the hydroxyl deformation mode.

The Raman spectrum of väyrynenite in the 300 to 800 cm\(^{-1}\) and in the 100 to 300 cm\(^{-1}\) spectral regions are displayed in Figures 5a and 5b. This spectrum (Figure 5a) may be subdivided into sections. The first section is the 700 to 800 cm\(^{-1}\) region, the bands centred upon 600 cm\(^{-1}\); the bands around 500 cm\(^{-1}\) and the bands between 300 and 400 cm\(^{-1}\). Raman bands at 573, 599, 619 and 642 cm\(^{-1}\) are assigned to the \(\nu_4\) PO\(_4^{3-}\) bending modes. The Raman bands at 463, 506 and 538 cm\(^{-1}\) are due to the \(\nu_2\) PO\(_4^{3-}\) bending modes. Raman bands at 707, 741 and 769 cm\(^{-1}\) are assigned to the out-of-plane vibrations of POH units. Farmer [23] tabled this band at 750 cm\(^{-1}\). In the infrared spectrum (Figure 4b), infrared bands are observed at 749 and 800 cm\(^{-1}\). The Raman bands at 334, 353, 381 and 404 cm\(^{-1}\) are attributed to metal-oxygen stretching bands. The Raman bands in the 100 to 300 cm\(^{-1}\) spectral range are assigned to lattice vibrations. Prominent bands are observed at 123, 184 and 232 cm\(^{-1}\).

The Raman and infrared spectra of väyrynenite in the 2600 to 3800 cm\(^{-1}\) spectral region is presented in Figure 6a and 6b. The Raman spectrum of väyrynenite is dominated by an intense Raman band at 3219 cm\(^{-1}\). This band is assigned to the OH stretching vibration. The band is observed in the infrared spectrum as an intense band at 3212 cm\(^{-1}\). In the
Raman spectrum, low intensity bands are found at 3315, 3388 and 3474 cm\(^{-1}\). The infrared spectrum displays an intense band at 3212 cm\(^{-1}\). There are distinct shoulder bands at 3166 and 3345 cm\(^{-1}\). The Raman and infrared spectra in the 1300 to 2000 cm\(^{-1}\) spectral range are illustrated in Figure 7a and 7b. Raman bands are observed at 1660, 1768 and 1802 cm\(^{-1}\). The band at 1660 cm\(^{-1}\) is assigned to the water bending mode. The infrared spectrum suffers from a lack of signal; nevertheless infrared bands may be found at 1487, 1675 and 1758 cm\(^{-1}\).

CONCLUSIONS

We have analysed väyrynenite a rare beryllium and manganese hydroxy phosphate mineral of general formula MnBe(PO$_4$)(OH,F) using electron microscope with an electron probe and vibrational spectroscopic techniques. Väyrynenite is a rare beryllium and manganese hydroxy phosphate mineral. The chemical formula using EMP/WDS techniques was found to be (Mn$_{0.88}$,Fe$_{0.08}$,Mg$_{0.01}$)$_{0.97}$Be$_{1.02}$(PO$_4$)$_{1.00}$(OH)$_{1.02}$.

Multiple Raman bands are observed in the PO$_4^{3-}$ $\nu_1$ symmetric stretching region at 986, 1004, 1009 cm\(^{-1}\) and multiple PO$_4^{3-}$ $\nu_3$ antisymmetric stretching modes are found at 1044, 1074, 1126, 1139 and 1186 cm\(^{-1}\). Such multiplicity of stretching modes suggests that there are non-equivalent phosphate units in the väyrynenite structure. Such a concept is supported by the multiple phosphate bending modes. Raman bands at 573, 599, 619 and 642 cm\(^{-1}\) are assigned to the $\nu_4$ PO$_4^{3-}$ bending modes. The Raman bands at 463, 506 and 538 cm\(^{-1}\) are due to the $\nu_2$ PO$_4^{3-}$ bending modes. An intense Raman band at 3219 cm\(^{-1}\) is assigned to the OH stretching vibration. Vibrational spectroscopy offers a mechanism
for the assessment of the molecular structure of väyrynenite. The infrared spectrum in the
OH stretching region, displays an intense band at 3212 cm\(^{-1}\) with shoulder bands at 3166
and 3345 cm\(^{-1}\).

ACKNOWLEDGEMENTS

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 CAPES – Conselho
Nacional de Desenvolvimento Científico e Tecnológico (grant No. 306287/2012-9).

REFERENCES


Figure 1. Backscattered electron image (BSI) of a väyrynenite single crystal up to 1.0 mm in length.
Figure 2. EDS analysis of väyrynenite.
Figure 3a Raman spectrum of väyrynenite (upper spectrum) and Figure 3b infrared spectrum of väyrynenite (lower spectrum)
Figure 4a Raman spectrum of väyrynenite (upper spectrum) in the 800 to 1300 cm\(^{-1}\) spectral range and Figure 4b infrared spectrum of väyrynenite (lower spectrum) in the 500 to 1300 cm\(^{-1}\) spectral range.
Figure 5a Raman spectrum of väyrynenite (upper spectrum) in the 300 to 800 cm\(^{-1}\) spectral range and Figure 5b Raman spectrum of väyrynenite (lower spectrum) in the 100 to 300 cm\(^{-1}\) spectral range.
Figure 6a Raman spectrum of väyrynenite (upper spectrum) in the 2600 to 3800 cm\(^{-1}\) spectral range and Figure 6b infrared spectrum of väyrynenite (lower spectrum) in the 2600 to 3800 cm\(^{-1}\) spectral range.
Figure 7a Raman spectrum of väyrynenite (upper spectrum) in the 1400 to 2000 cm\(^{-1}\) spectral range and Figure 7b infrared spectrum of väyrynenite (lower spectrum) in the 1300 to 1800 cm\(^{-1}\) spectral range.
Table 1. Chemical composition of väyrynennite from the Viitaniemi pegmatite (mean of 5 electron microprobe analyses). H₂O and BeO calculated by stoichiometry. (*) http://rruff.info/doclib/hom/vayrynenite.pdf.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P₂O₅</th>
<th>MnO</th>
<th>FeO</th>
<th>As₂O₅</th>
<th>BeO</th>
<th>CaO</th>
<th>MgO</th>
<th>H₂O</th>
<th>Na₂O</th>
<th>Al₂O₃</th>
<th>PbO</th>
<th>CuO</th>
<th>BaO</th>
<th>ZrO</th>
<th>SrO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAB-103</td>
<td>39.49</td>
<td>35.06</td>
<td>3.15</td>
<td>0.02</td>
<td>14.22</td>
<td>0.14</td>
<td>0.19</td>
<td>5.12</td>
<td>0.04</td>
<td>0.02</td>
<td>14.22</td>
<td>0.14</td>
<td>0.01</td>
<td>0.09</td>
<td>0.21</td>
<td>98.01</td>
</tr>
<tr>
<td>Viitaniemi pegmatite*</td>
<td>39.98</td>
<td>34.01</td>
<td>5.92</td>
<td>-</td>
<td>13.85</td>
<td>0.53</td>
<td>-</td>
<td>5.12</td>
<td>0.20</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100.11</td>
</tr>
<tr>
<td>Chitral*</td>
<td>40.05</td>
<td>38.40</td>
<td>3.40</td>
<td>-</td>
<td>12.2</td>
<td>0.07</td>
<td>-</td>
<td>5.38</td>
<td>0.03</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100.00</td>
</tr>
<tr>
<td>MnBe(PO₄)(OH)*</td>
<td>40.34</td>
<td>40.32</td>
<td>0.00</td>
<td>0.00</td>
<td>14.22</td>
<td>0.00</td>
<td>0.00</td>
<td>5.12</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>P</th>
<th>Mn</th>
<th>Fe</th>
<th>As</th>
<th>Be</th>
<th>Ca</th>
<th>Mg</th>
<th>OH</th>
<th>Na</th>
<th>Al</th>
<th>Pb</th>
<th>Cu</th>
<th>Ba</th>
<th>Zr</th>
<th>Sr</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAB-103</td>
<td>1.00</td>
<td>0.88</td>
<td>0.08</td>
<td>0.00</td>
<td>1.02</td>
<td>0.00</td>
<td>0.01</td>
<td>1.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>Viitaniemi pegmatite*</td>
<td>0.99</td>
<td>0.85</td>
<td>0.15</td>
<td>-</td>
<td>0.98</td>
<td>0.02</td>
<td>-</td>
<td>1.00</td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.02</td>
</tr>
<tr>
<td>Chitral*</td>
<td>1.02</td>
<td>0.97</td>
<td>0.08</td>
<td>-</td>
<td>0.87</td>
<td>0.00</td>
<td>-</td>
<td>1.07</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.01</td>
</tr>
<tr>
<td>MnBe(PO₄)(OH)*</td>
<td>1.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.00</td>
<td></td>
</tr>
</tbody>
</table>