ABSTRACT

Samples of manganese-rich rock containing two compositional varieties of tokyoite in association with noélbensonite were retrieved from a drill core obtained from the Postmasburg area in the Northern Cape Province of South Africa. The samples consist of fine-grained braunite, hematite, and hausmannite. Within this material abundant vugs are observed that are filled with witherite, baryte, and barytocalcite. In addition, As-rich tokyoite, tokyoite, and noélbensonite occur in the center of the vugs, in fine aggregates 0.1 to 1 mm in size. Individual As-rich tokyoite grains are typically 20–200 μm in size. The outer walls of the vugs are lined with microcrystalline K-feldspar, witherite, and/or sérandite. Textural evidence of the Ba-rich mineral phases in association with As-rich tokyoite suggest an epigenetic mode of formation of the observed assemblages, caused by V- and As-bearing alkali-rich fluids interacting with pre-existing Mn-rich minerals.

Electron microprobe analysis (EMPA), electron backscatter diffraction analysis (EBSD), and Raman spectroscopy show that the As-rich tokyoite is a mineral belonging to the brackebuschite mineral group. Its measured mineral composition corresponds to the formula \( (\text{Ba}_{1.92}\text{Sr}_{0.05}\text{Pb}_{0.03})\text{S}_{2.00}((\text{Mn}^{3+}_{0.98}\text{Fe}^{3+}_{0.02})\text{S}_{1.00}[(\text{As}_{1.05}\text{V}_{0.95}\text{S}_{2.00}\text{O}_{8})](\text{OH})) \). Electron backscatter diffraction analysis results point to a monoclinic, \( P2_1/m \) space group, with cell parameters \( a = 9.121 \) Å, \( b = 6.142 \) Å, \( c = 7.838 \) Å, \( \beta = 112^\circ \), \( Z = 2 \). The structure is therefore similar to gamagarite. Raman spectra of As-rich tokyoite were compared to spectra of arsenbrackebuschite and arsentsumebite, and those of noélbensonite to spectra of hennomartinite and lawsonite. The indexing of Raman peaks in As-rich tokyoite, by similarity with arsentsumebite, suggests a possible ordering of the AsO₄ and VO₄ tetrahedra. This observation, correlated with mineral chemistry and specifically an As:V ratio of \( \sim 1:1 \), suggest that the As-rich tokyoite may in fact represent a possible new mineral with ordering of As and V at tetrahedral positions, or at least an unknown As analogue of tokyoite.

**Keywords:** tokyoite, As-rich tokyoite, noélbensonite, Raman, EMPA, EBSD, South Africa.

INTRODUCTION

The Northern Cape Province of South Africa is endowed with a large and diverse set of rare minerals associated with the commercial iron and manganese deposits that characterize the region. The Kalahari manganese field (KMF; Figure 1), and particularly the northernmost area thereof containing high-grade manganese ores of the Hotazel Formation (Wessels and N’chwaning mines; Astrup & Tsikos 1998), is host to many such minerals (Cairncross & Beukes 2013). The diversity of minerals found in the KMF is also highlighted by Gutzmer & Beukes (1996a), who list no less than 135 different species, including such rare minerals as banalsite, kentrolite, kornite, sérandite, armbrusterite, norrishite, and sugilite. Further south, in the broad area between the towns of Kathu and Postmasburg, lies the Postmasburg manganese field (PMF; Fig. 1), where a similarly impressive variety of minerals is found in association with karst-hosted
manganese deposits developed on dolomitic carbonate rocks of the Campbellrand Subgroup. These deposits have also been described by various authors (e.g., Hall 1926, Nel 1929, du Toit 1933, de Villiers 1944, 1960, Plehwe-Leisen & Klemm 1995, Gutzmer & Beukes 1996b), particularly with respect to their complex and diverse mineralogy. In one of the most recent such studies, Moore et al. (2011) described a complex assemblage of minerals near the Bruce iron-ore mine in the northern part of the PMF. Here sugilite, armbrusterite, albite, sérandite, witherite, and norriellite occur in the footwall to conglomeratic iron-ores that typify the locality.

De Villiers (1943) discovered in the PMF the rare barium–manganese vanadate gamagarite, Ba$_2$(Fe$^{3+}$, Mn$^{3+}$)(VO$_4$)$_2$(OH), which forms part of the brackebuschite structural group of minerals (Matsubara et al. 2004). Tokyoite, Ba$_2$Mn$^{3+}$(VO$_4$)$_2$(OH), was first described by Matsubara et al. (2004) from the (now abandoned) Shiromaru manganese mine in Japan. Its structure is similar to gamagarite, which belongs to the brackebuschite group. These authors found tokyoite in association with braunite, hematite, albite, aegirine, celsian, hyalophane, and rare minerals such as cymrite and tamaite. They also described veinlets of banalsite, baryte, strontianite, sérandite, piemontite-(Sr), marstonite, and ganophyllite-group minerals. The tokyoite at the type locality occurs as very fine aggregates, and is thought to have formed as a result of alkali-rich, Ba- and V-bearing circulating fluids reacting with pre-existing assemblages containing braunite (Matsubara et al. 2004).

This paper presents the first occurrence of tokyoite and noëlbensonite on the African continent and the first occurrence ever of As-rich tokyoite. In order to define the structural properties of tokyoite, its As-rich variety, and noëlbensonite, and their compositions, we used a combination of micro-Raman spectroscopy, electron microprobe microanalyses (EMPA), and electron backscatter diffraction (EBSD). The measured As content in As-rich tokyoite indicates a possible new mineral, with V and As ordered at different sites.

**Geological Setting**

Manganese ore deposits of the PMF were first discovered near the town of Postmasburg in the early part of the 20th century and soon became South Africa’s most important commercial resource of manganese (Gutzmer & Beukes 1996b). Some of the historically major manganese mines in the area are those at Lohatlha, Glossam, and Bishop (Astrup & Tsikos 1998). The discovery and subsequent exploitation of the giant KMF saw the gradual decline of mining in the PMF, which today occurs only on a relatively small-scale (Gutzmer & Beukes 1996b).

A regional anticlinal structure known as the Maremane Dome occurs in Northern Cape Province between the towns of Postmasburg to the south and Kathu to the north (Fig. 1). The Maremane Dome consists, for most part, of dolomitic carbonate rocks of the Campbellrand Subgroup (Moore et al. 2011). The PMF occurs in two belts along a 65 km long, broadly N–S transect across the Maremane Dome (De Villiers 1960, Gutzmer & Beukes 1996b, Astrup & Tsikos 1998), referred to as the Western and Eastern Belts. The ferruginous-type ores of the Western Belt occur within paleo-sinkholes in the chert-free Reivilo Formation of the Campbellrand Subgroup (Plehwe-Leisen & Klemm 1995, Gutzmer & Beukes 1996b). The fact that the manganese ores rest directly on the Reivilo Formation and contain little to no chert is testament to the chert-free nature of the substrate (Gutzmer & Beukes 1996b).

Mineralogically, the Eastern Belt ores range from fine-grained bixbyite- and braunite-rich to massive and highly vuggy bixbyite-rich ores. The siliceous ores of the Eastern Belt are intimately associated with the Wolhaarkop chert breccia and the Fairfield Formation of the Campbellrand Subgroup (Plehwe-Leisen & Klemm 1995, Gutzmer & Beukes 1996b). The matrix of the breccia is composed of quartz, hematite, and braunite, becoming more siliceous and ferruginous toward the top and more manganiferous toward the base.

Gutzmer & Beukes (1996b) describe the transition zones between chert breccia and manganese ore bodies of the Eastern Belt as gradual and characterized by a rapid increase in the manganiferous matrix to chert fragment ratio. Cross-cutting veins of coarse baryte and globular hematite, as well as pyrolusite, have been described, as well as replacement of chert fragments by baryte (Gutzmer & Beukes 1996b). The mineable manganese ores predominantly consist of massive braunite and tend to be found at the contact between the chert breccia and the underlying dolomite (Gutzmer & Beukes 1996b). Whereas mixed ore-types to the aforementioned two endmembers are also reported, they are generally considered akin to those of the Eastern Belt (Plehwe-Leisen & Klemm 1995).

**Sample Selection**

Samples with As-rich tokyoite were retrieved from a drill core provided by Kumba Iron Ore (a member of the Anglo American Group) and obtained from the broader Kolomela area near the town of Postmasburg in the Northern Cape Province of South Africa. The general drill core location is indicated in Figure 1. The drill core intersects a lithological interval of laminated, massive, and vuggy manganese-rich lithologies at the interface between minor, laminated hematite-rich mineralization, and the Wolhaarkop Breccia stratigraphically below (Fig. 1). The stratigraphy intersected in the studied drill-core therefore bears similarities to the one from the Bruce iron-ore mine studied for its intricate mineralogy by Moore et al. (2011). The greatest modal abundance of As-rich tokyoite and noëlbensonite occurs towards the basal, vuggy ferro-manganiferous part of the examined intersection, between 95 and 97 m depth below the present surface (Fig. 1).
Optical examination of petrographic polished thin sections with transmitted, polarized light was conducted at Rhodes University, Department of Geology, using an Olympus BX60 microscope equipped with a 5 Mega-pixel PAXCam digital camera. Preliminary identification of minerals was done at the Electron Microscopy Unit (EMU) at Rhodes University, using a Scanning Electron Microscope (SEM; TESCAN Vega TS 5136LM) equipped with an Si(Li) EDS INCAPentaFET-x3 detector. Energy-dispersive spectroscopy (EDS) data and images were processed using the Oxford Instruments INCA Energy350 software. The analytical conditions for the EDS analysis were: accelerating voltage 20 kV, quantitative optimization on Co, dead time 40–45%, and acquisition rate 3.9–4.2 × 10^3 counts/s.

Electron probe micro-analysis data were obtained at the Department of Geology, Rhodes University, using a JEOL JXA 8230 Superprobe equipped with four WD spectrometers and operated at 15 kV and 20 nA with a beam size of ~1 μm. Wavelength-dispersive spectroscopy (WDS) qualitative scans were performed for several (As-rich) tokyite grains in order to identify the elements present in measurable concentrations. The Virtual WDS software was used to simulate possible interferences between elements to be analyzed. The counting time for most elements was set to 10 s per peak and 5 s per background, except for Pb, S, P, and

**FIG. 1.** Regional geological map of the Postmasburg manganese field with approximate location of the studied drill-core site and log information for the intersected Fe- and Mn-rich rocks.
Sr, where a higher counting time was used in order to improve detection limits (20 s per peak and 10 s for lower and upper backgrounds, respectively). Natural standards and ZAF correction matrices were employed for quantification.

Raman spectra were obtained at Ecole Normale Supérieure de Lyon using a multichannel Raman microprobe (LabRam HR800 from DILOR) equipped with a confocal microscope configuration (incident laser beam 514.53 nm line of Ar ion laser focused to less than 2 μm in diameter). The scattered Raman light is focused through a 100 μm slit into a spectograph equipped with a 1800 lines/mm grating and analyzed by a CCD detector, giving a resolution of approximately 2.5 cm⁻¹. The accumulation times for Raman spectra were typically 60–120 s. Precision on the Raman peak positions is typically 0.2 cm⁻¹ for strong peaks, whereas accuracy is 1 cm⁻¹.

Electron backscatter diffraction analysis was performed at Pascal University, Clermont-Ferrand, France, using a JEOL 5910 LV scanning electron microscope, equipped with a Bruker Quantax system, with Eflash EBSD camera coupled with an EDS-SDD Xflash detector. Analytical conditions were: low vacuum of 10 Pa, working distance 30 mm, tilt 70°, emission current 90 μA. The error of the best fit between the match unit and the experimental EBSD patterns is 5%.

RESULTS AND INTERPRETATION

Optical examination

Tokyoite, Ba₂Mn³⁺[(V,As)O₄]₂(OH), As-rich tokyoite, Ba₂Mn³⁺[(As,V)O₄]₂(OH), and noélbensonite, BaMn³⁺₂(Si₂O₇)(OH)₂·(H₂O), occur associated with each other as minute, reddish, pink-reddish, and brown-reddish grains, respectively, dispersed in fine (0.1 to 1 mm) vug-filling aggregates. Individual grains are usually 20–200 μm in size. The minerals making up the vug fillings include variable proportions of quartz, K-feldspar, sérandite–pektolite, noélbensonite, aegirine, albite, natrolite, paragonite, witherite, and baryte, and minor strontianite, piemontite, barytocalcite, and calcite. The matrix consists of varying amounts of braunite, hematite, and hausmannite.

In thin sections (PPL mode), tokyoite and As-rich tokyoite have a reddish-brown to pinkish dark red color.

Fig. 2. A series of petrographic images (A–D) in plane-polarized light, illustrating typical mineralogical associations and textural relationships of tokyoite (Tk), As-rich tokyoite (As-Tk), and noélbensonite (Nbn), as observed in selected samples from this study (see text for detailed discussion). Associated phases: Kfs = K-feldspar with adularia habit; Srd = sérandite; Qz = quartz.
Tokyoite, As-rich Tokyoite, and Noélbensonite

(fig. 2A–D). The As-rich tokyoite and tokyoite show distinct pleochroism with absorption from yellowish or brownish red to pinkish dark red, respectively. With increasing As/V ratio, the absorption color of tokyoite becomes darker red. Petrographic evidence suggests that As-rich varieties of tokyoite (dark red to pinkish dark red) have replaced As-poor ones (reddish brown), whereas sérandite and noélbensonite seem to develop on the exterior of tokyoite grains (Fig. 2A–B). Kawachi et al. (1996) found noélbensonite replacing sérandite in the Woods mine, New South Wales (Australia). Our samples show a rather reverse relationship, in which noélbensonite grows later on the exterior of the tokyoite grains (Fig. 2A). The tokyoite and As-rich tokyoite (and possibly noélbensonite as well) are replaced or overgrown by sérandite (Fig. 2A–B). The outer walls of the tokyoite-bearing vugs are lined with microcrystalline K-feldspar (adularia habit, Figs. 2A and C), sérandite, and occasionally the barium carbonate mineral witherite. In some vugs, the tokyoite appears to be replaced by quartz along cleavage planes (Fig. 2D).

Mineral composition of tokyoite, As-rich tokyoite, and noélbensonite

Energy-dispersive spectroscopy and electron microprobe analyses revealed two different data sets for tokyoite—one of which is As-rich—which also correlate with two different phases having slightly different optical properties and representing two different textural contexts. The backscattered images (Figs. 3A–D) do not show any obvious difference in contrast between As-poor tokyoite and As-rich tokyoite. Figure 3A shows anhedral tokyoite with noélbensonite and sérandite grown at the exterior of the tokyoite grains. Baryte and witherite are also associated with tokyoite (Fig. 3B). In most cases, relics of tokyoite along with lesser witherite are invaded by K-feldspar (adularia; Fig. 3C), or can be embedded in...
quartz, where partial and crystallographically controlled replacement of tokyoite by quartz can be observed (Fig. 3D). The only way in which As-rich tokyoite can be confidently detected within the (As-poor) tokyoite is by careful investigation of the WDS element maps (e.g., As map of Fig. 4 and Supp. Fig. A1), where small, heterogeneous spots of As-rich areas can be observed in the tokyoite grains.

A first EMPA quantitative data set (Table 1 and Supplementary Table A1) shows an As-poor tokyoite (throughout this text referred to simply as “tokyoite”), where V > As per formula unit. This phase appears as a relict in the vugs and seems to be heterogeneous replaced (Figs. 2A–B, 4) by a second generation of As-rich tokyoite (As \( \text{apfu} \geq V \text{ apfu} \); Table 1 and Supp. Table A2). The calculated formulae of tokyoite and As-rich tokyoite, normalized to 8.5 oxygens per formula unit are:

(As-poor) tokyoite:

\[
(Ba_{1.95}Pb_{0.04}Sr_{0.01})_{\Sigma 2.00} (Mn^{3+}_{0.97}Fe^{3+}_{0.03})_{\Sigma 1.00} [\text{Si}_{1.75}O_{2.50}]_{\Sigma 2.00} \text{OH} \]

As-rich tokyoite:

\[
(Ba_{1.92}Sr_{0.05}Pb_{0.03})_{\Sigma 2.00} (Mn^{3+}_{0.98}Fe^{3+}_{0.02})_{\Sigma 1.00} [\text{Si}_{1.05}V_{0.95}]_{\Sigma 2.00} \text{OH} \]

The strong negative correlation between As and V (Fig. 5) clearly suggests that the two elements occupy equivalent tetrahedral crystallographic sites, suggesting a continuous solid solution between tokyoite (V endmember) and a theoretical As endmember (not known). However, a significant gap can be observed in the distribution of V and As (Fig. 5), raising the possibility of a miscibility gap between the above-mentioned endmembers. Interestingly for this occurrence, both tokyoite and As-rich tokyoite can accommodate small amounts of Pb (replacing Ba), and minor Fe\(^{3+}\) replacing Mn\(^{3+}\), but only the As-rich tokyoite was found to accommodate measurable Sr replacing Ba. Moreover, even though PbO and Fe\(_2\)O\(_3\) occur in minor amounts in tokyoite, a very weak positive correlation can be inferred between the two (not shown), suggesting a limited solution between tokyoite and arsenbrackebuschite, Pb\(_2\)Fe\(^{3+}\)(AsO\(_4\))\(_2\)(OH)\(_2\). The crystal chemistry of tokyoite and As-rich tokyoite thus opens the way to the assessment of miscibility between Ba/Mn vanadates and Ba/Mn arsenates.

Noëlbensonite, a rare Ba–Mn silicate of the lawsonite structure type, has a composition presented in the EMPA data of Table 1 and Supplementary Table A3. Minor Sr (up to 0.13 \( \text{apfu} \)) and Ca (up to 0.04 \( \text{apfu} \)) can substitute for Ba, and minor Fe\(^{3+}\) (up to 0.01 \( \text{apfu} \)) can substitute for Mn\(^{3+}\). The formula of noëlbensonite, normalized to eight oxygen atoms per formula unit is:

\[
(Ba_{0.85}Sr_{0.13}Ca_{0.04})_{\Sigma 1.02} (Mn^{3+}_{1.98}Fe^{3+}_{0.01})_{\Sigma 1.99} \text{Si}_{1.95}V_{0.04}O_7(\text{OH})_2 \cdot H_2O
\]

The composition of our noëlbensonite is very close to that described by Kawachi et al. (1996) from the Woods mine in New South Wales, Australia, with the only notable difference being the high vanadium content (up to 1.3 wt.% \( V_2O_5 \)) in the noëlbensonite described herein.

**Raman spectroscopy**

The present work presents for the first time the Raman spectra of As-rich tokyoite and noëlbensonite (Figs. 6 and 7). The spectrum of As-rich tokyoite is compared with the Raman spectra of arsenbrackebuschite, Pb\(_2\)Fe\(^{3+}\)(AsO\(_4\))\(_2\)(OH) (RRUFF\textsuperscript{TM} Project, RuffID 110041), and arsensumebite, Pb\(_2\)Cu(AsO\(_4\))(SO\(_4\))(OH), from Frost et al. (2011). The comparison of multiple spectra was done with the CrystalSleuth software (Laetsch & Downs 2006). By comparison of Raman peaks for other minerals in the garnagrite group, the following indexation of the vibration bands can be made (sometimes with a certain degree of uncertainty, marked below with a question mark): the 170 and 241 cm\(^{-1}\) band corresponds to Ba–O lattice vibrations, peaks at 308–340 cm\(^{-1}\) are attributed to (AsO\(_4\))\(^{3-}\) bending modes, the peak at 390 cm\(^{-1}\) probably corresponds to SrO stretching vibrations, and the peaks at 442–460 cm\(^{-1}\) represent (AsO\(_4\))\(^{3-}\) and (VO\(_4\))\(^{3-}\) bending modes and partially overlap doubly degenerate \( v_2 \) (SO\(_4\))\(^{2-}\) in arsensumebite (420 cm\(^{-1}\)) and arsenbrackebuschite (464 cm\(^{-1}\)). The peaks at 540–554 cm\(^{-1}\) are attributed to (PO\(_4\))\(^{3-}\) \( v_4 \) bands and the peaks at 604–620 cm\(^{-1}\) representing \( v_4 \) bands bending modes of (SO\(_4\))\(^{2-}\) are missing in As-rich tokyoite. The peak at 730 cm\(^{-1}\) is attributed to the (AsO\(_4\))\(^{3-}\) bending mode(?) while the peak
TABLE 1. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF TOKYOITE, AS-RICH TOKYOITE, AND NOÉLBENSONITE (OXIDES IN wt.%)

<table>
<thead>
<tr>
<th>Mineral tokyoite</th>
<th>As-rich tokyoite</th>
<th>noélbensonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis</td>
<td>23-32</td>
<td>23-34</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>25.91</td>
<td>28.19</td>
</tr>
<tr>
<td>As₂O₅</td>
<td>5.95</td>
<td>3.99</td>
</tr>
<tr>
<td>SiO₂</td>
<td>bd</td>
<td>bd</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>13.17</td>
<td>13.24</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.29</td>
<td>0.37</td>
</tr>
<tr>
<td>BaO</td>
<td>50.86</td>
<td>51.52</td>
</tr>
<tr>
<td>PbO</td>
<td>0.84</td>
<td>0.80</td>
</tr>
<tr>
<td>SrO</td>
<td>0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>CaO</td>
<td>bd</td>
<td>bd</td>
</tr>
<tr>
<td>H₂O*</td>
<td>2.77</td>
<td>1.60</td>
</tr>
<tr>
<td>Total**</td>
<td>97.23</td>
<td>98.40</td>
</tr>
</tbody>
</table>

| Cations normalized to 8.5 O apfu | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|----------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| V⁵⁺                              | 1.688| 1.801| 1.598| 1.668| 0.89 | 0.91  | 0.845| 0.978 | 0.957 | 0.117 | 0.067 | 0.033 | 0.036 | 0.038 | 0.011 |
| As⁵⁺                             | 0.307| 0.202| 0.396| 0.329| 0.088| 1.090 | 1.163| 1.041 | 1.047 | 0.128 | 0.001 | 0.000 | 0.000 | 0.001 | 0.001 |
| Si                               | 0.000| 0.000| 0.000| 0.003| 0.004| 0.014 | 0.006| 0.005 | 0.013 | 0.020 | 1.918 | 1.940 | 1.970 | 1.950 | 0.014 |
| Mn³⁺                             | 0.988| 0.975| 0.961| 0.977| 0.013| 0.924 | 0.941| 0.914 | 0.940 | 0.019 | 1.974 | 1.996 | 1.962 | 1.984 | 0.013 |
| Fe³⁺                             | 0.021| 0.027| 0.048| 0.027| 0.014| 0.003 | 0.016| 0.025 | 0.019 | 0.008 | 0.004 | 0.006 | 0.000 | 0.005 | 0.004 |
| Ba                               | 1.965| 1.953| 1.952| 1.951| 0.010| 1.889 | 1.939| 1.916 | 1.917 | 0.026 | 0.855 | 0.872 | 0.856 | 0.848 | 0.037 |
| Pb                               | 0.022| 0.021| 0.040| 0.032| 0.006| 0.042 | 0.027| 0.036 | 0.034 | 0.013 | 0.000 | 0.002 | 0.010 | 0.003 | 0.003 |
| Sr                               | 0.012| 0.016| 0.010| 0.011| 0.003| 0.090 | 0.053| 0.068 | 0.060 | 0.014 | 0.155 | 0.139 | 0.127 | 0.126 | 0.031 |
| Ca                               | -     | -     | -     | -     | -    | 0.012 | 0.004| 0.006 | 0.004 | 0.003 | 0.016 | 0.021 | 0.033 | 0.042 | 0.023 |
| Total                            | 5.003| 4.995| 5.005| 4.998| 0.005| 4.983 | 4.993| 4.989 | 4.991 | 0.015 | 4.990 | 5.009 | 4.994 | 4.997 | 0.006 |

*H₂O estimated by difference;
**Total oxides (wt.%) without H₂O. SD = standard deviation 1σ. bd = below detection limit.
Means and SD: for 16 analyses of tokyoite, 15 analyses of As-rich tokyoite, and 10 analyses of noélbensonite, respectively (See Supp. Tables A1, A2, and A3). P₂O₅, SO₃, Al₂O₃, and K₂O concentrations are below detection limits and were eliminated from the table above.
Fig. 5. (A) Strong negative correlation between As and V (apfu) in tokyoite, suggesting a possible miscibility gap between tokyoite and As-rich tokyoite.

at 814–827 cm$^{-1}$ represents the (AsO$_4$)$^{3-}$/v1 symmetric stretching mode. The peak at 846 cm$^{-1}$ is attributed to the (AsO$_4$)$^{3-}$/asymmetric stretching mode(?), and the peak at 906 cm$^{-1}$ represents (VO$_3$)$^{3-}$ and (AsO$_4$)$^{3-}$/units of v1 symmetric stretching modes. The peak at 935 cm$^{-1}$ can be attributed to the v1 symmetric stretching mode for H–(VO$_3$)$^{3-}$/or (HOVO$_3$)$^{3-}$/and/or H–(AsO$_4$)$^{3-}$/or (HOAsO$_3$)$^{2-}$/units(?). Other possible interpretations include a shifting of O–V–O stretching modes owing to stronger bonding due to the small amount of SO$_4$ analyzed(?). The peak at 972 cm$^{-1}$ is assigned to the (SO$_4$)$^{2-}$/v1 symmetric stretching mode.

The four outstanding peaks between 830 cm$^{-1}$ and 935 cm$^{-1}$, a pair between 830–846 cm$^{-1}$, and a pair between 906 and 935 cm$^{-1}$, could have two possible explanations. (1) The peaks at 830 and 846 cm$^{-1}$ evidently originate from the As–O stretching vibrations within the AsO$_4$ group (the strong one is from the symmetrical stretching vibrations and relatively weak one at 846 cm$^{-1}$ from the asymmetrical stretching vibrations). When plotting the Raman data for arsenbrackebuschite against As-rich tokyoite data, one can see that these two peaks overlap quite well. The two peaks of As-rich tokyoite at 870 and 930 cm$^{-1}$, however, do not match those for V–O stretching vibrations in brackebuschite (spectrum not shown in Fig. 6); they are at much higher wave numbers. This shift could suggest that the bonding for V–O is stronger than expected for the VO$_4$ group in this mineral. The stronger V–O bonding could be achieved by weaker bonds of additional cations (Ca, Ba, Mn$^{3+}$) to the oxygen apices of VO$_4$ tetrahedra or, less likely, by minor replacement of the tetrahedrally coordinated cation (e.g., P$^{5+}$, S$^{6+}$, or Cr$^{6+}$), which were not found in our samples. We can also assume that some type of Jahn-Teller distortion characteristic of octahedral Mn$^{3+}$ may be responsible for the observed shift in frequency. (2) VO$_4$ and AsO$_4$ groups in our sample may actually be ordered. In other words, they may occupy two

Fig. 6. Raman spectra of As-rich tokyoite (this study), arsenbrackebuschite (RUUFF sample 100184), and arsensumeite (after Frost et al. 2011). Peak assignment: 170 and 241 cm$^{-1}$: Ba–O lattice vibrations; 308–340 cm$^{-1}$: (AsO$_4$)$^{3-}$/bending modes; 390 cm$^{-1}$: SrO stretching vibrations(?); 442–460 cm$^{-1}$: (AsO$_4$)$^{3-}$/and (VO$_4$)$^{3-}$/bending modes, partially overlapping doubly degenerate v2 (SO$_4$)$^{2-}$/in arsensumeite (420 cm$^{-1}$) and arsenbrackebuschite (464 cm$^{-1}$); 540–554 cm$^{-1}$: (PO$_4$)$^{3-}$/v4 bands and the peaks at 604–620 cm$^{-1}$ representing v4 bands bending modes of (SO$_4$)$^{2-}$/are missing in As-rich tokyoite; 730 cm$^{-1}$: (AsO$_4$)$^{3-}$/v5 bending mode(?); 814–827 cm$^{-1}$: (AsO$_4$)$^{3-}$/v1 symmetric stretching mode; 846 cm$^{-1}$: (AsO$_4$)$^{3-}$/asymmetric stretching mode(?); 906 cm$^{-1}$: (VO$_4$)$^{3-}$/and (AsO$_4$)$^{3-}$/units of v1 symmetric stretching modes; 935 cm$^{-1}$: v1 symmetric stretching mode for H–(VO$_4$)$^{3-}$/or (HOVO$_3$)$^{3-}$/and/or H–(AsO$_4$)$^{3-}$/or (HOAsO$_3$)$^{2-}$/units(?). See text for further interpretations.

Fig. 7. Raman spectra of noëlbensonite (this study), hennomartinite (RRUFF Project, RRUFF ID R130039), and lawsonite (RRUFF Project, RRUFF ID R050042). Peak assignment: 160 and 185 cm$^{-1}$ and a bigger peak at 245 cm$^{-1}$/; Ba–O bending vibrations in noëlbensonite; ~170 cm$^{-1}$/and ~300 cm$^{-1}$/; Sr–O bending vibration in hennomartinite. Single peak at ~386 cm$^{-1}$/; stretching mode of Mn–O, common in noëlbensonite and hennomartinite and missing in lawsonite. 436 cm$^{-1}$/; Al–O stretching mode in lawsonite. Peaks between 500 and 600 cm$^{-1}$/; Si–O bonding, with shifting and splitting of these peaks in noëlbensonite and hennomartinite probably due to the presence of Mn$^{3+}$/; 650, 660, and 696 cm$^{-1}$/; stretching vibrations of Ba–O, Sr–O, and Ca–O molecules, in noëlbensonite, hennomartinite, and lawsonite, respectively. 935 cm$^{-1}$/; Si–O stretching vibration.
distinct crystallographic positions, as in arsentsumebite (AsO$_4$ versus SO$_4$) or in bushmakinite (PO$_4$ versus VO$_4$).

The Raman spectrum of noélbensonite was compared with the spectra of: (1) a Sr-analogue with the lawsonite structure called hennomartinite (RRUFF$^{20}$ Project, RRUFF ID R130039), and (2) lawsonite (RRUFF$^{21}$ Project, RRUFF ID R050042) (Fig. 7). The main Raman peaks in noélbensonite are (in order of increasing Raman shift): 160 and 185 cm$^{-1}$, 245 cm$^{-1}$, a pair of asymmetric peaks at 385 and 435 cm$^{-1}$, a prominent peak at 523 cm$^{-1}$ with an acute shoulder at 572 cm$^{-1}$, a smaller but acute peak at 650 cm$^{-1}$, followed by a significant peak at 935 cm$^{-1}$ having a small shoulder at 904 cm$^{-1}$. One minor peak occurs at 1065 cm$^{-1}$. We present here a possible assignment of the peaks to various types of molecule and vibration (for all three minerals compared in Fig. 7).

The peaks situated at 160 and 185 cm$^{-1}$, and a bigger peak at 245 cm$^{-1}$, are attributed to Ba–O bending vibrations in noélbensonite. In hennomartinite, the flat peak at ca. 170 cm$^{-1}$ and ~300 cm$^{-1}$ is assigned to Sr–O bending vibrations. The single peak seen at ~386 cm$^{-1}$ represents the stretching mode of Mn–O, common in noélbensonite and hennomartinite and missing in lawsonite. The peak at 436 cm$^{-1}$ is attributed to the Al–O stretching mode. The most interesting are the prominent peaks between 500 and 600 cm$^{-1}$: here, the peaks of noélbensonite and hennomartinite are split in two, but asymmetrically to each other. The prominent side of the hennomartinite peak at 562 cm$^{-1}$ overlaps perfectly the peak of lawsonite. All these peaks represent stretching vibrations of Si–O bonding, with shifting and splitting of these peaks in noélbensonite and hennomartinite probably due to the presence of Mn$^{3+}$. This could be a possible effect of Jahn-Teller distortion characteristic of octahedral Mn$^{3+}$. The peaks at 650, 660, and 696 cm$^{-1}$ are attributed to the stretching vibrations of Ba–O, Sr–O, and Ca–O molecules in noélbensonite, hennomartinite, and lawsonite, respectively. The prominent peak at 935 cm$^{-1}$ represents the Si–O stretching vibration, being common for all three investigated silicate phases.

**Summary and Conclusions**

A new occurrence of tokyoite and noélbensonite and a first occurrence of As-rich tokyoite from the Postmasburg area of South Africa has been presented and described. The EBSD, Raman, and EMPA data illustrate that As-rich tokyoite is a mineral belonging to the brackebuschite mineral group. The EBSD results suggest a monoclinic, $P2_1/m$ space group, and cell parameters $a$ 9.121, $b$ 6.142, and $c$ 7.838 Å, $\alpha = \gamma = 90^\circ$, $\beta = 112^\circ$, which are similar to the cell parameters of gamagarite ($a$ 9.174, $b$ 6.164, and $c$ 7.882 Å, $\alpha = \gamma = 90^\circ$, $\beta = 112.9^\circ$, RRUFF ID R130111) and tokyoite ($a$ 9.104, $b$ 6.132, and $c$ 7.895 Å, $\alpha = \gamma = 90^\circ$, $\beta = 112.2^\circ$, see Matsubara et al. 2004). The results clearly show that As-rich tokyoite is a mineral of the gamagarite group. The EBSD pattern for noélbensonite (not shown) was compared against the structure of lawsonite, CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O, with space group $Cmcm$ and cell parameters $a$ 8.795 Å, $b$ 5.847 Å, $c$ 13.142 Å, $\alpha = \beta = \gamma = 90^\circ$. The match between the pattern observed and that of lawsonite further confirmed that our mineral is in fact noélbensonite.

**Electron backscatter diffraction**

The grain size of tokyoite, As-rich tokyoite, and noélbensonite is very small, commonly below 100 µm. The extremely small size, coupled with the observed complex relationships of replacement and intergrowth rendered physically impossible the separation of a single crystal for X-ray diffraction or other structural techniques. Instead, we opted for comparing the indexed EBSD patterns of our minerals with EBSD patterns of known minerals that have similar symmetry and cell parameters. The EBSD pattern obtained for As-rich tokyoite (not shown) was indexed and compared against its best fit, namely gamagarite, Ba$_2$(Fe$^{3+}$,Mn$^{3+}$)$_2$(VO$_4$)$_2$(OH) (VO$_4$)$_2$(OH). The results show that As-tokyoite has a monoclinic $P2_1/m$ space group and cell parameters with best fit $a$ 9.121, $b$ 6.142, and $c$ 7.838Å, $\alpha = \gamma = 90^\circ$, $\beta = 112^\circ$, which are similar to the cell parameters of gamagarite ($a$ 9.174, $b$ 6.164, and $c$ 7.882 Å, $\alpha = \gamma = 90^\circ$, $\beta = 112.9^\circ$, RRUFF ID R130111) and tokyoite ($a$ 9.104, $b$ 6.132, and $c$ 7.895 Å, $\alpha = \gamma = 90^\circ$, $\beta = 112.2^\circ$, see Matsubara et al. 2004). The discovery of tokyoite and As-rich tokyoite from the Postmasburg area of South Africa has been presented and described. The EBSD, Raman, and EMPA data illustrate that As-rich tokyoite is a mineral belonging to the brackebuschite mineral group. The EBSD results suggest a monoclinic, $P2_1/m$ space group, and cell parameters $a$ 9.121, $b$ 6.142, and $c$ 7.838 Å, $\alpha = \gamma = 90^\circ$, $\beta = 112^\circ$. The structure of As-tokyoite is similar to that of gamagarite and tokyoite. The Raman spectrum of As-rich tokyoite was compared to spectra of arsenbrackebuschite and arsentsumebite. The comparison with arsentsumebite suggests a possible ordering of the AsO$_4$ and VO$_4$ tetrahedra. This observation, correlated with mineral compositions, indicates that the As-rich tokyoite may represent a new mineral with ordering of As and V and formula Ba$_2$Mn$_3^{3+}$[(AsO$_4$)$\times$(VO$_4$)](OH), or an unknown As-analogue of tokyoite with formula Ba$_2$Mn$_3^{3+}$[(As,V)O$_4$]$_2$(OH). Further structural investigation of grains of suitable size and purity will be required to resolve that uncertainty.

The occurrence of Sr-bearing noélbensonite in the PMF described herein can suggest that the Sr/Ba ratio of the alkali-rich brines responsible for its formation was lower than that of the hydrothermal fluids forming its Sr-analogue, hennomartinite, SrMn$_3^{3+}$Si$_2$O$_7$(OH)$_2$·H$_2$O, described from the Wessels mine of the KMF (Armbruster et al. 1993). The discovery of tokyoite and As-rich tokyoite in vug-fills of manganese-rich rocks of the wider PMF, in conjunction with the occurrence of gamagarite in similar rocks as previously identified by De Villiers (1943), provide an exciting new window into the natural diversity of the brackebuschite mineral group. The complexity of the mineral assemblage with which the tokyoite and As-rich tokyoite are associated is also similar to that described from Mn-rich rocks near the Bruce iron ore mine by Moore et al. (2011). The similarities between the two assemblages, combined with the new information presented in this paper, and particularly the multitude of Ba-bearing phases observed, such as noélbensonite and witherite, further suggest that the alkali-rich brines thought to be responsible for the observed mineral paragenesis were also V- and As-bearing. This further reinforces the
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