KHOMYAKOVITE AND MANGANOKHOMYAKOVITE, TWO NEW MEMBERS OF THE EUDIALYTE GROUP FROM MONT SAINT-HILAIRE, QUEBEC, CANADA

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ABSTRACT

Khomyakovite, ideally $Na_{12}Sr_3Ca_6Fe_3Zr_3W(Si_{25}O_{73})(O,OH,H_2O)_3(OH,Cl)_2$ and manganokhomyakovite, ideally $Na_{12}Sr_3Ca_6Mn_3Zr_3W(Si_{25}O_{73})(O,OH,H_2O)_3(OH,Cl)_2$ are two new members of the eudialyte group from Mont Saint-Hilaire, Quebec. They occur as orange to orange-red, pseudo-octahedral crystals ranging in size from 0.5 mm (khomyakovite) to 5 mm (manganokhomyakovite). Associated minerals include, for khomyakovite: analcime, annite, calcite, natrolite, pyrite, and titanite, and for manganokhomyakovite: aegirine, albite, analcime, annite, cerussite, galena, kupletskite, microcline, molybdenite, natrolite, pyrite, pyrrhotite, sodalite, sphalerite, titanite, wöhlerite and zircon. Both minerals are transparent to translucent, with a vitreous luster and white streak. They are brittle, with a hardness of 5–6 (Mohs scale). They have no cleavage, no parting and an uneven fracture. They are uniaxial negative, for khomyakovite: $\omega = 1.6279(5)$ and $\varepsilon = 1.6254(5)$, and for manganokhomyakovite: $\omega = 1.629(1)$ and $\varepsilon = 1.626(2)$. They are trigonal, space group $R3m$. For khomyakovite: a 14.2959(8), c 30.084(3) Å, V 5324.6(7) $Å^3$, and for manganokhomyakovite: a 14.282(3), c 30.12(1) Å, V 5320(3) $Å^3$, $Z = 3$. The strongest X-ray powder-diffraction lines, measured for manganokhomyakovite [d in Å (I)(hkl)], are 11.500(90)(101), 9.535(70)(012), 6.452(50)(104), 6.072(50)(021), 5.735(50)(202), 3.406(50)(131), 3.213(50)(208), 3.167(50)(217), 2.980(100)(315) and 2.856(80)(404). The infrared spectrum of manganokhomyakovite is given. An electron-microprobe analysis of the khomyakovite crystal used for single-crystal work gave Na_2O 11.35, K_2O 0.52, MgO 0.04, CaO 10.42, MnO 1.63, FeO 4.33, SrO 8.45, Al_2O_3 0.09, La_2O_3 0.21, Ce_2O_3 0.18, SiO_2 43.70, TiO_2 0.11, ZrO_2 10.62, HfO_2 0.18, Nb_2O_5 1.33, Ta_2O_5 0.02, WO_3 3.80, Cl 0.67, H_2O 0.87, O ≡ Cl 0.15, total 98.37 wt.%. The proportion of H_2O was calculated by stoichiometry from the structure analysis. The empirical formula of khomyakovite, based on 78.70 anions as determined in the structure analysis, is $(Na_{12.26}Ca_{0.33}K_{0.38}Sr_{0.13}REE_{0.08})_{\Sigma13.05}$ $(Sr_{2.78}Na_{0.22})_{\Sigma3}$ Ca_6 $(Fe_{2.05}Mn_{0.78}Mg_{0.03})_{\Sigma2.86}$ $(Zr_{2.94}Ti_{0.05}Hf_{0.03})_{\Sigma3.02}$ $(W_{0.56}Nb_{0.34})_{\Sigma0.90}$ $(Si_{24.78}Al_{0.06})_{\Sigma24.84}$ O_{73} $(O,OH,H_2O)_{\Sigma3.70}$ $(OH_{1.36}Cl_{0.64})_{\Sigma2}$. For manganokhomyakovite, an average of four electron-microprobe analyses gave Na_2O 10.37 (10.05–10.59), K_2O 0.41 (0.37–0.45), CaO 10.20 (10.08–10.35), MnO 4.21 (3.91–4.38), FeO 2.58 (2.40–2.65), SrO 9.17 (8.63–9.63), Al_2O_3 0.02 (0.00–0.05), La_2O_3 0.12 (0.00–0.27), Ce_2O_3 0.20 (0.00–0.30), SiO_2 42.98 (42.51–43.39), TiO_2 0.02 (0.00–0.07), ZrO_2 10.43 (10.40–10.50), HfO_2 0.17 (0.16–0.19), Nb_2O_5 1.58 (1.35–2.05), Ta_2O_5 0.03 (0.00–0.05), WO_3 4.48 (3.66–4.83), Cl 0.84 (0.78–0.89), H_2O 0.83, O ≡ Cl 0.19, total 98.45 wt. %. The proportion of H_2O was calculated by stoichiometry from the crystal-structure relationship with khomyakovite, confirmed by TGA and IR data. The empirical formula of manganokhomyakovite, based on 78.70 anions as found in the crystal structure of khomyakovite, is $(Na_{11.51}K_{0.30}Ca_{0.25}Sr_{0.04}REE_{0.07})_{\Sigma12.17}$ Sr_3 Ca_6 $(Mn_{2.04}Fe_{1.23})_{\Sigma3.27}$ $(Zr_{2.91}Hf_{0.03}Ti_{0.01})_{\Sigma2.95}$ $(W_{0.66}Nb_{0.41}Ta_{0.01})_{\Sigma1.08}$ $(Si_{24.60}Al_{0.01})_{\Sigma24.61}$ O_{73} $(O,OH,H_2O)_{3.70}$ $(OH_{1.19}Cl_{0.81})_{\Sigma2}$. For khomyakovite, $D_{calc.} = 3.14$ g/cm³, and for manganokhomyakovite, $D_{calc.} = 3.17$ g/cm³, $D_{meas.} = 3.13(3)$ g/cm³. Both minerals possess the eudialyte structure. Single-crystal data for khomyakovite show that W dominates over Nb in $M(3)$, and Sr over Na in $Na(4)$. $M(2)$ is dominated by Fe in khomyakovite, and by Mn in manganokhomyakovite.

Keywords: khomyakovite, manganokhomyakovite, eudialyte, new mineral species, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La khomyakovite, dont la composition idéale est $Na_{12}Sr_3Ca_6Fe_3Zr_3W(Si_{25}O_{73})(O,OH,H_2O)_3(OH,Cl)_2$, et la manganokhomyakovite, $Na_{12}Sr_3Ca_6Mn_3Zr_3W(Si_{25}O_{73})(O,OH,H_2O)_3(OH,Cl)_2$, sont deux nouveaux membres du groupe de l'eudialyte découverts au Mont Saint-Hilaire, Québec. Ils se présentent en cristaux orange à orange rougeâtre pseudo-octaédriques allant de 0.5 mm (khomyakovite) à 5 mm (manganokhomyakovite). Parmi les minéraux associés, on trouve, pour la khomyakovite, analcime, annite, calcite, natrolite, pyrite, et titanite, et pour la manganokhomyakovite, aegirine, albite, analcime, annite, cérussite, galène, kupletskite, microcline, molybdénite, natrolite, pyrite, pyrrhotite, sodalite, sphalérite, titanite, wöhlerite et zircon. Les deux minéraux sont transparents ou translucides, avec un éclat vitreux et une rayure blanche. Ils sont cassants, et ont une dureté de 5 à 6 (échelle de Mohs). Ils sont sans clivage, sans plan de séparation, et ont une cassure inégale. Les deux sont uniaxes négatifs; pour la khomyakovite, $\omega = 1.6279(5)$ et $\varepsilon = 1.6254(5)$, et pour la manganokhomyakovite, $\omega = 1.629(1)$ et $\varepsilon = 1.626(2)$. Ces minéraux sont trigonaux, groupe spatial $R3m$. Les paramètres réticulaires de la khomyakovite sont a 14.2959(8), c 30.084(3)

Å, V 5324.6(7) Å^3, et ceux de la manganokhomyakovite sont a 14.282(3), c 30.12(1) Å, V 5320(3) Å^3, $Z = 3$. Les raies les plus intenses du spectre de la manganokhomyakovite en diffraction X, méthode des poudres [d en Å $(I)(hkl)$], sont 11.500(90)(101), 9.535(70)(012), 6.452(50)(104), 6.072(50)(021), 5.735(50)(202), 3.406(50)(131), 3.213(50)(208), 3.167(50)(217), 2.980(100)(315) et 2.856(80)(404). Nous présentons le spectre infra-rouge de la manganokhomyakovite. Une analyse du cristal de khomyakovite utilisé pour l'ébauche de la structure a donné Na$_2$O 11.35, K$_2$O 0.52, MgO 0.04, CaO 10.42, MnO 1.63, FeO 4.33, SrO 8.45, Al$_2$O$_3$ 0.09, La$_2$O$_3$ 0.21, Ce$_2$O$_3$ 0.18, SiO$_2$ 43.70, TiO$_2$ 0.11, ZrO$_2$ 10.62, HfO$_2$ 0.18, Nb$_2$O$_5$ 1.33, Ta$_2$O$_5$ 0.02, WO$_3$ 3.80, Cl 0.67, H$_2$O 0.87, O $\equiv$ Cl 0.15, total 98.37% par poids. La proportion de H$_2$O a été calculée par stoechiométrie dictée par l'analyse de la structure. La formule empirique de la khomyakovite, fondée sur une base de 78.70 anions telle qu'indiquée par l'analyse structurale, est (Na$_{12.26}$Ca$_{0.33}$K$_{0.38}$Sr$_{0.13}$$REE_{0.08}$)$_{\Sigma13.05}$(Sr$_{2.78}Na_{0.22}$)$_{\Sigma3}Ca_6$(Fe$_{2.05}Mn_{0.78}Mg_{0.03}$)$_{\Sigma2.86}$(Zr$_{2.94}Ti_{0.05}Hf_{0.03}$)$_{\Sigma3.02}$(W$_{0.56}Nb_{0.34}$)$_{\Sigma0.90}$(Si$_{24.78}Al_{0.06}$)$_{\Sigma24.84}$ O$_{73}$ (O,OH,H$_2$O)$_{\Sigma3.70}$ (OH$_{1.36}$Cl$_{0.64}$)$_{\Sigma2}$. Pour la manganokhomyakovite, la moyenne des résultats de quatre analyses à la microsonde électronique est Na$_2$O 10.37 (10.05–10.59), K$_2$O 0.41 (0.37–0.45), CaO 10.20 (10.08–10.35), MnO 4.21 (3.91–4.38), FeO 2.58 (2.40–2.65), SrO 9.17 (8.63–9.63), Al$_2$O$_3$ 0.02 (0.00–0.05), La$_2$O$_3$ 0.12 (0.00–0.27), Ce$_2$O$_3$ 0.20 (0.00–0.30), SiO$_2$ 42.98 (42.51–43.39), TiO$_2$ 0.02 (0.00–0.07), ZrO$_2$ 10.43 (10.40–10.50), HfO$_2$ 0.17 (0.16–0.19), Nb$_2$O$_5$ 1.58 (1.35–2.05), Ta$_2$O$_5$ 0.03 (0.00–0.05), WO$_3$ 4.48 (3.66–4.83), Cl 0.84 (0.78–0.89), H$_2$O 0.83, O $\equiv$ Cl 0.19, total 98.45% (par poids). La proportion de H$_2$O a été calculée par stoechiométrie à partir de la relation structurale avec la khomyakovite, telle que confirmée par analyses thermogravimétrique différentielle et infra-rouge. La formule empirique de la manganokhomyakovite, fondée sur une base de 78.70 anions selon les résultats structuraux sur la khomyakovite, serait (Na$_{11.51}$K$_{0.30}$Ca$_{0.25}$Sr$_{0.04}$$REE_{0.07}$)$_{\Sigma12.17}$ Sr$_3$ Ca$_6$ (Mn$_{2.04}$Fe$_{1.23}$)$_{\Sigma3.27}$ (Zr$_{2.91}$Hf$_{0.03}$Ti$_{0.01}$)$_{\Sigma2.95}$ (W$_{0.66}$Nb$_{0.41}$Ta$_{0.01}$)$_{\Sigma1.08}$ (Si$_{24.60}$Al$_{0.01}$)$_{\Sigma24.61}$ O$_{73}$ (O,OH,H$_2$O)$_{3.70}$ (OH$_{1.19}$Cl$_{0.81}$)$_{\Sigma2}$. Pour la khomyakovite, $D_{calc.}$ = 3.14 g/cm^3, et pour la manganokhomyakovite, $D_{calc.}$ = 3.17 g/cm^3, $D_{mes.}$ = 3.13(3) g/cm^3. Les deux minéraux possèdent la structure de l'eudialyte. Les données obtenues sur un cristal unique de khomyakovite montrent que le tungstène est prédominant par rapport au Nb dans le site M(3), et le strontium est plus important que le Na dans le site Na(4). Le site M(2) contient surtout du fer dans la khomyakovite, et du manganèse dans la manganokhomyakovite.

(Traduit par la Rédaction)

Mots-clés: khomyakovite, manganokhomyakovite, eudialyte, nouvelles espèces minérales, structure, Mont Saint-Hilaire, Québec.

INTRODUCTION

A systematic study of the chemical composition of the Na-rich zirconosilicate eudialyte (Johnsen & Gault 1997) revealed a wide variation in composition. To fully understand the structure of this complex mineral, 20 specimens representative of the spectrum of compositions were selected for crystal-structure analysis (Johnsen & Grice 1999). One of those selected, here described as khomyakovite, contains appreciable amounts of Sr. The structure analysis not only confirmed the dominant presence of Sr in one of the *Na* sites, but also revealed the presence of another cation in the *Nb* site whose identity had not been established in the early analytical work. Subsequent electron-microprobe analysis showed this element to be tungsten, unexpected in the chemical spectrum of eudialyte-group minerals.

Owing to the paucity of material (only two crystals less than 0.5 mm in diameter), and because of the unusual mode of occurrence, a miarolitic cavity in nepheline syenite, a search was conducted of similar material in an attempt to locate more specimens. No further khomyakovite was found. However, its manganese analogue, manganokhomyakovite, was discovered at this time and in greater quantity.

The purpose of this paper is to describe these two new members of the eudialyte group, khomyakovite and manganokhomyakovite, and their occurrence in the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec. Khomyakovite is named in honor of Dr. Alexander Petrovich Khomyakov (b. 1933), of the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Moscow, Russia, for his extensive contributions to the mineralogy and geochemistry of alkaline rocks, in particular those of agpaitic character. His work on the mineralogy of the Lovozero and Khibina massifs is renowned, and he has been involved in the discovery of more than seventy mineral species. Manganokhomyakovite is the manganese analogue of khomyakovite.

The new minerals and their names were approved by the Commission on New Minerals and Mineral Names, IMA. The holotype specimen of khomyakovite (catalogue no. CMNMC 81557) and the cotype specimens of manganokhomyakovite (catalogue nos. CMNMC 81558 and CMNMC 81559) are housed in the collection of the Canadian Museum of Nature in Ottawa.

OCCURRENCE

Mont Saint-Hilaire is an alkaline intrusive complex and one of the ten Monteregian Hills, a series of genetically related plutons aligned along the St. Lawrence Valley for almost 150 km eastward from Oka to Megantic in the province of Quebec. Mont Saint-Hilaire has become well known for its diversity in mineral species (Horváth & Gault 1990); indeed, this diversity is also exhibited in the wide chemical variation in the eudialyte-group minerals from this locality.

A single specimen of khomyakovite, now designated as the holotype, was collected in 1988 by museum staff from a small miarolitic cavity (5 cm in diameter) in

nepheline syenite in the Poudrette quarry, Mont Saint-Hilaire. Associated minerals are analcime, annite, calcite, natrolite, pyrite and titanite. Eudialyte-group minerals are relatively common at Mont Saint-Hilaire. However, they are quite rare in this association. Owing to the lack of material required to complete our investigation, we conducted a search of various collections and put out a request to the collecting community for eudialyte from this association. László and Elsa Horváth, private collectors from Hudson, Quebec, subsequently found similar material in their collection; it proved to be the manganese analogue of khomyakovite. The cotype specimens of manganokhomyakovite were collected by the Horváths in 1976 from a 15 cm miarolitic cavity in the Demix quarry. The manganokhomyakovite is associated with aegirine, albite, analcime, annite, cerussite, galena, kupletskite, microcline, molybdenite, natrolite, pyrite, pyrrhotite, sodalite, sphalerite, titanite, wöhlerite and zircon. The Demix and Poudrette quarries, at one time separate, are now one entity, the Poudrette quarry.

Since the original identification of the Horváth material, several other specimens received from collectors have been confirmed as manganokhomyakovite. All are from miarolitic cavities in nepheline syenite. However, khomyakovite remains elusive, and only one grain, less than 0.5 mm in diameter, remains from our study. Tungsten has been noted in only one other species at Mont Saint-Hilaire, scheelite (Horváth & Gault 1990). Only one specimen of scheelite has been found. Its presence as 1–2 mm grains in a miarolitic cavity in nepheline syenite attests to the scarcity of tungsten at Mont Saint-Hilaire. Tungsten has been detected only in trace amounts in eudialyte-group minerals from other associations at Mont Saint-Hilaire.

PHYSICAL AND OPTICAL PROPERTIES

Khomyakovite and manganokhomyakovite occur as orange to orange-red, transparent to translucent, pseudo-octahedral crystals (Fig. 1) ranging in size from 0.5 mm (khomyakovite) to 5 mm (manganokhomyakovite). For manganokhomyakovite, forms measured by reflecting goniometer include $\{0001\}$, $\{11\bar{2}0\}$, $\{02\bar{2}1\}$, $\{10\bar{1}1\}$ and $\{01\bar{1}2\}$ (Fig. 2). They have a white streak and vitreous luster. Both are brittle, with no cleavage, no parting and an uneven fracture. The minerals have a Mohs hardness of 5–6, and do not fluoresce in either short- or long-wave ultraviolet light. The density of manganokhomyakovite, measured by suspension in methylene iodide, is 3.13(3) g/cm^3, which compares well with the calculated density of 3.17 g/cm^3. The density of

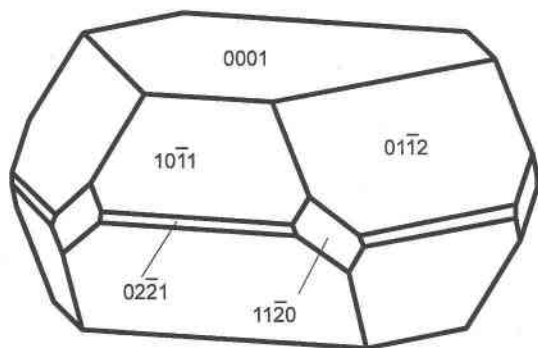FIG. 1. Manganokhomyakovite crystals (0.5–1 mm). Photo by L. Horváth.

FIG. 2. Idealized drawing of manganokhomyakovite crystal, showing observed forms.

khomyakovite could not be measured owing to lack of material. Its calculated density is 3.14 g/cm^3.

Khomyakovite is uniaxial negative, $\omega = 1.6279(5)$ and $\varepsilon = 1.6254(5)$; manganokhomyakovite is uniaxial negative, $\omega = 1.629(1)$ and $\varepsilon = 1.626(2)$. Both have moderate pleochroism; in khomyakovite, ε is pale yellow and ω is yellow-orange; in manganokhomyakovite, ε is yellow and ω is orange-yellow. Gladstone–Dale calculations give a compatibility index of –0.005 for khomyakovite and 0.013 for manganokhomyakovite; these values are regarded as superior (Mandarino 1981).

CHEMICAL COMPOSITION

Chemical analyses were done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine in XMAQNT (pers. commun., C. Davidson, CSIRO). The operating voltage was 15 kV, and the beam current was 20 nA. Owing to the size of the khomyakovite grain, only a 20 μm beam diameter was employed, whereas a 40 μm beam was used for the analysis of manganokhomyakovite. The migration and volatilization of sodium in eudialyte are not a significant problem with a defocused beam; on the other hand, a volatilization problem with the vlasovite standard on which Na, Si and Zr were calibrated was recognized and corrected. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. Forty-six elements were sought, but only those detected are reported here. The presence of H_2O was confirmed in manganokhomyakovite by infrared spectroscopy. The following standards were used in the electron-microprobe analyses: vlasovite (Na$K\alpha$, Si$K\alpha$, Zr$L\alpha$), sanidine (K$K\alpha$), diopside (Ca$K\alpha$, Mg$K\alpha$), celestite (Sr$L\alpha$), tephroite (Mn$K\alpha$), almandine (Fe$K\alpha$), chrysoberyl (Al$K\alpha$), synthetic LaPO$_4$ (La$L\alpha$), synthetic CePO$_4$ (Ce$L\alpha$), rutile (Ti$K\alpha$), synthetic hafnon (Hf$L\alpha$), synthetic MnNb$_2$O$_6$ (Nb$L\alpha$), synthetic NiTa$_2$O$_6$ (Ta$L\alpha$),

synthetic CoWO$_4$ (W$M\alpha$) and marialite (Cl$K\alpha$). Data for elements in the standards were collected for 50 s or 0.25% precision, whichever was attained first. For khomyakovite, two analyses were performed on two separate grains. The composition of the grain chosen for a structure analysis is reported here, along with the range in composition: Na$_2$O 11.35 (10.75–11.35), K$_2$O 0.52 (0.48–0.52), MgO 0.04 (0.04–0.05), CaO 10.42 (10.34–10.42), MnO 1.63 (1.14–1.63), FeO 4.33 (4.33–4.75), SrO 8.45 (8.45–8.89), Al$_2$O$_3$ 0.09 (0.05–0.09), La$_2$O$_3$ 0.21 (0.09–0.21), Ce$_2$O$_3$ 0.18 (0.15–0.18), SiO$_2$ 43.70 (43.56–43.70), TiO$_2$ 0.11 (0.11–0.11), ZrO$_2$ 10.62 (10.62–10.83), HfO$_2$ 0.18 (0.18–0.22), Nb$_2$O$_5$ 1.33 (0.88–1.33), Ta$_2$O$_5$ 0.02 (0.00–0.02), WO$_3$ 3.80 (3.80–4.16), Cl 0.67 (0.67–0.77), H$_2$O 0.87, O ≡ Cl 0.15, total 98.37 wt.%. The proportion of H$_2$O was calculated by stoichiometry from the results of the crystal-structure analysis. The empirical formula of khomyakovite, based on 78.70 anions as determined in the structure analysis, is (Na$_{12.26}$Ca$_{0.33}$K$_{0.38}$Sr$_{0.13}$$REE_{0.08}$)$_{\Sigma 13.05}$ (Sr$_{2.78}$Na$_{0.22}$)$_{\Sigma 3}$ Ca$_6$ (Fe$_{2.05}$Mn$_{0.78}$Mg$_{0.03}$)$_{\Sigma 2.86}$ (Zr$_{2.94}$Ti$_{0.05}$Hf$_{0.03}$)$_{\Sigma 3.02}$ (W$_{0.56}$Nb$_{0.34}$)$_{\Sigma 0.90}$ (Si$_{24.78}$Al$_{0.06}$)$_{\Sigma 24.84}$ O$_{73}$ (O,OH, H$_2$O)$_{\Sigma 3.70}$(OH$_{1.36}$Cl$_{0.64}$)$_{\Sigma 2}$ or, ideally, Na$_{12}$Sr$_3$Ca$_6$Fe$_3$Zr$_3$ W(Si$_{25}$O$_{73}$) (O,OH,H$_2$O)$_3$ (OH)$_2$.

For manganokhomyakovite, the average results of four analyses, with ranges, are: Na$_2$O 10.37 (10.05–10.59), K$_2$O 0.41 (0.37–0.45), CaO 10.20 (10.08–10.35), MnO 4.21 (3.91–4.38), FeO 2.58 (2.40–2.65), SrO 9.17 (8.63–9.63), Al$_2$O$_3$ 0.02 (0.00–0.05), La$_2$O$_3$ 0.12 (0.00–0.27), Ce$_2$O$_3$ 0.20 (0.00–0.30), SiO$_2$ 42.98 (42.51–43.39), TiO$_2$ 0.02 (0.00–0.07), ZrO$_2$ 10.43 (10.40–10.50), HfO$_2$ 0.17 (0.16–0.19), Nb$_2$O$_5$ 1.58 (1.35–2.05), Ta$_2$O$_5$ 0.03 (0.00–0.05), WO$_3$ 4.48 (3.66–4.83), Cl 0.84 (0.78–0.89), H$_2$O 0.83, O ≡ Cl 0.19, total 98.45 wt. %. The proportion of H$_2$O was calculated by stoichiometry from the results of the crystal-structure analysis of khomyakovite. The empirical formula of manganokhomyakovite, based on 78.70 anions from the structure analysis of khomyakovite, is (Na$_{11.51}$K$_{0.30}$ Ca$_{0.25}$Sr$_{0.04}$$REE_{0.07}$)$_{\Sigma 12.17}$ Sr$_3$ Ca$_6$ (Mn$_{2.04}$Fe$_{1.23}$)$_{\Sigma 3.27}$ (Zr$_{2.91}$Hf$_{0.03}$Ti$_{0.01}$)$_{\Sigma 2.95}$ (W$_{0.66}$Nb$_{0.41}$Ta$_{0.01}$)$_{\Sigma 1.08}$ (Si$_{24.60}$Al$_{0.01}$)$_{\Sigma 24.61}$ O$_{73}$ (O,OH,H$_2$O)$_{3.70}$ (OH$_{1.19}$Cl$_{0.81}$)$_{\Sigma 2}$ or, ideally, Na$_{12}$Sr$_3$Ca$_6$Mn$_3$Zr$_3$W(Si$_{25}$O$_{73}$) (O,OH,H$_2$O)$_3$ (OH)$_2$. A thermogravimetric analysis of manganokhomyakovite indicated a slight loss of H$_2$O, but it was too small to measure.

INFRARED ANALYSIS

The infrared spectrum of manganokhomyakovite (Fig. 3) was obtained using a Bomem Michelson MB–120 Fourier transform infrared spectrometer with a diamond anvil cell as a microsampling device. The broad absorption bands at 3514 and 1621 cm^{-1} are assigned to the [OH] stretching mode and the [H$_2$O] bending mode, respectively. The three small peaks at 1421, 1463 and 1506 cm^{-1} are attributed to the stretching mode of a [CO$_3$] group. Although the amount of
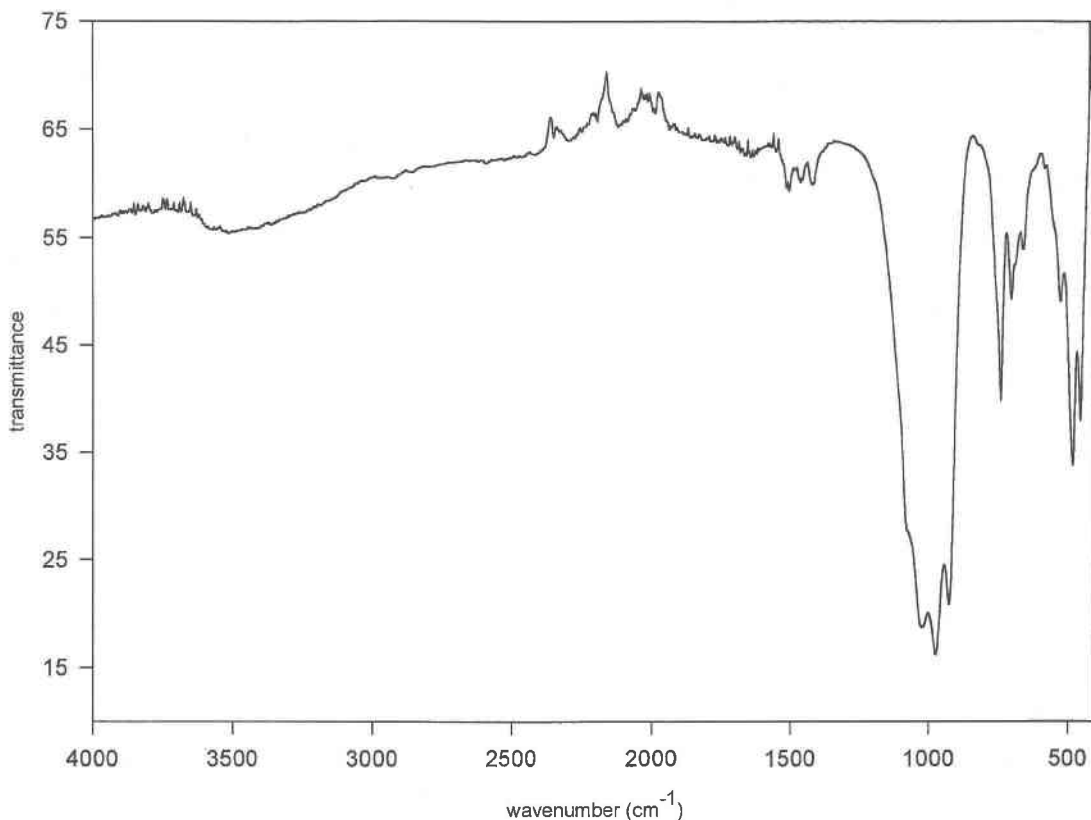
FIG. 3.   Infrared spectrum of manganokhomyakovite.

(CO_3) is small, it is sufficient to register on the IR spectrum, which is extremely sensitive to the presence of any molecular vibration modes of a crystal. These spectra are also noted in oneillite (Johnsen *et al*. 1999) and kentbrooksite (Johnsen *et al* 1998). The (CO_3) group can be accommodated within the crystal structure at the $X1$ site. Note that the disordered $X1$ site has bond lengths $X1a - X1b$ of 1.26(2) Å in a trigonal array (bond angle 117.9[6]°), much like that of a (CO_3) group. The three peaks at 926, 976 and 1023 cm^{-1} are assigned to the symmetric stretching of [SiO_4] and indicate considerable splitting of the [SiO_4] vibration modes, attributable to a structure with more than one crystallographically distinct [SiO_4] group. Peaks at 660, 703 and 741 cm^{-1} are assigned to the bending of [SiO_4]. Peaks at 455, 483 and 526 cm^{-1} could not be unequivocally assigned, but are likely due to the larger polyhedra, with bond distances greater than 2 Å.

X-Ray Crystallography and Crystal-Structure Determination

X-ray powder-diffraction data of manganokhomyakovite collected with a 114.6-mm diameter Debye–Scherrer camera using Cu$K\alpha$ (Ni-filtered) radiation are given in Table 1. Corresponding data for khomyakovite were poor owing to limited material. However, a calculated pattern based on crystal-structure data is practically identical with that of manganokhomyakovite.

The single crystal of khomyakovite used for the collection of X-ray-diffraction intensity data is a ground sphere of 0.12 mm diameter. Intensity data were collected on a Siemens fully automated four-circle diffractometer operated at 50 kV and 40 mA with graphite-monochromated Mo$K\alpha$ radiation. A set of 25 reflections were used to center the crystal and refine the cell parameters. We first assumed a non-centrosymmetric rhombohedral cell, and collected one asymmetric unit of intensity data (*i.e.*, $+ h + k \pm l$) to $2\theta = 60°$ using a $\theta{:}2\theta$ scan-mode, with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. The data collection consisted of approximately 3800 reflections with more than 85% observed (*i.e.*, $F_o > 4\sigma\ F_o$). Information relevant to the data collection and structure determination is given in Table 2.

For the ellipsoidal absorption correction, 10 to 14 intense diffraction-maxima in the range 12 to 60° 2θ were chosen for Ψ diffraction-vector scans after the

TABLE 1. MANGANOKHOMYAKOVITE: X-RAY POWDER DIFFRACTION DATA

I/I_o	d_{obs}	d_{calc}(Å)	h k l	I/I_o	d_{obs}	d_{calc}(Å)	h k l
90	11.500	11.441	1 0 1			2.380	3 3 0
10	10.120	10.040	0 0 3	30	2.378	2.377	4 1 6
70	9.530	9.558	0 1 2	10	2.325	2.330	2 4 1
50	6.450	6.432	1 0 4	1	2.269	2.266	2 3 8
50	6.070	6.058	0 2 1	25	2.141	2.140	3 1 11
50	5.735	5.721	2 0 2	10	2.062	2.065	3 2 10
<1	5.417	5.416	0 1 5	<1	2.013	2.015	3 4 2
<1	5.004	5.020	0 0 6	30	1.984	1.986	4 2 8
40	4.319	4.315	2 0 5	10	1.940	1.940	3 3 9
30	4.112	4.123	3 0 0	20	1.909	1.912	0 5 10
40	3.971	3.972	2 1 4			1.907	6 0 6
20	3.820	3.814	3 0 3	30	1.839	1.838	4 3 7
1	3.691	3.693	1 2 5			1.838	4 1 12
30	3.578	3.571	2 2 0			1.805	3 0 15
30	3.539	3.532	0 2 7	5	1.803	1.801	4 0 16
50	3.406	3.408	1 3 1			1.800	6 1 5
3	3.354	3.347	0 0 9	35	1.784	1.785	4 4 0
		3.345	3 1 2	5	1.768	1.766	0 4 14
50	3.213	3.216	2 0 8	<1	1.722	1.720	7 0 4
50	3.167	3.166	2 1 7	1	1.680	1.682	4 4 6
		3.030	1 1 9	1	1.649	1.650	1 3 16
20	3.028	3.029	0 4 2			1.650	2 6 5
100	2.980	2.981	3 1 5	1	1.629	1.629	1 1 18
15	2.912	2.910	2 2 6	5	1.607	1.608	4 0 16
80	2.856	2.860	4 0 4	3	1.550	1.551	3 0 18
<1	2.787	2.788	2 3 2			1.550	5 4 4
		2.708	0 2 10	4	1.482	1.481	2 7 4
5	2.701	2.699	4 1 0	1	1.466	1.466	2 4 16
5	2.656	2.655	3 2 4			1.466	7 2 5
30	2.598	2.598	3 0 9	3	1.433	1.434	0 0 21
20	2.534	2.536	3 1 8			1.433	1 2 20
		2.532	2 1 10	3	1.408	1.408	1 8 5
<1	2.516	2.511	4 0 7				

Debye-Scherrer 114.6 mm diameter powder camera, CuKα radiation, visually estimated intensities. Indexing based on cell: $a = 14.282(3)$, $c = 30.12(1)$ Å, $V = 5320(3)$ Å³.

method of North *et al.* (1968). The converging R for the Ψ-scan dataset decreased from 1.73% before the absorption correction to 1.34% after the absorption correction. The excellent convergence of R-values attests to the near-spherical shape of the crystal. Reduction of the intensity data, structure determination and initial refinement were done with the SHELXTL (Sheldrick 1990) package of computer programs. The final refinements were done with the SHELXL–93 program (Sheldrick 1993). The strategy applied to the final stages of the refinement is described in detail by Johnsen & Grice (1999).

TABLE 2. KHOMYAKOVITE: CRYSTAL DATA AND STRUCTURE REFINEMENT

Sample identification	Sample # 6 in Johnsen & Grice (1999)
Wavelength	0.71073 Å
Crystal system: space group	Trigonal: $R3m$
Unit-cell dimensions	$a = 14.2959(8)$, $c = 30.084(3)$ Å
Volume	5324.6(7) Å³
Crystal size	Sphere 0.12 mm in diameter
θ range for data collection	1.79 to 30.12°
Index ranges	$-17 \leq h \leq 10$, $-10 \leq k \leq 17$, $-42 \leq l \leq 42$
Reflections collected	3863
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3863 / 0 / 282
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma\ (I)$]	$R1 = 0.049$, $wR2 = 0.082$
R indices (all data)	$R1 = 0.079$, $wR2 = 0.093$
Isotropic refinement	$R1 / wR2$: 0.070 / 0.133
Largest diff. peak and hole	1.11 and -1.54 e·Å⁻³
ψ convergence before/after	1.73 / 1.34
$|E^2 - 1|$	0.790
Effect of TWIN command	$R1: 0.059 \rightarrow 0.049$

The final atomic coordinates and isotropic displacement parameters for the khomyakovite structure are presented by Johnsen & Grice (1999, sample #6). Lists of observed and calculated structure-factors, anisotropic displacement factors and selected bond-lengths have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Khomyakovite and manganokhomyakovite are members of the eudialyte group. As described by Johnsen & Grice (1999), the eudialyte structure consists of layers of six-membered rings of $[M(1)O_6]$ octahedra [mainly Ca in $M(1)$] linked together by $[M(2)O_n]$ polyhedra [Fe or Mn in $M(2)$] sandwiched between two pseudocentrosymmetrically related layers of three-membered and nine-membered silicate rings forming a 2:1 composite layer. The 2:1 composite layers are cross-linked by Zr in octahedral coordination and related to one another in accordance with the rhombohedral symmetry. This open structure is filled with five distinct $[Na\phi_n]$ polyhedra in which Na may have various coordinations. The $Na(4)$ site is particularly prone to incorporation of heavy elements such as the rare earths and Sr. The $M(3)$ and $Si(7)$ are central sites in the two crystallographically distinct nine-membered silicate rings, and related by the substitution: $^{[6]}M(3) + {}^{[4]}Si(7) \Leftrightarrow 2^{[4]}Si(7)$, in which $M(3)$ typically is occupied by Nb.

For the majority of the eudialyte-group minerals, the empirical formula is of the type: $Na_{15}[M(1)]_6[M(2)]_3Zr_3$ $[M(3)](Si_{25}O_{73})(O,OH,H_2O)_3(Cl,F,OH)_2$. The most prominent substitutions are revealed by the formulation of a solid-solution series between the classic eudialyte, rich in Si, Ca, Fe and Cl, and kentbrooksite (Johnsen *et al.* 1998), rich in Nb, *REE*, Mn and F. Khomyakovite and manganokhomyakovite differ from other members of the group in having W as the dominant element in $M(3)$ and Sr as the dominant element in $Na(4)$. The distinction between the two minerals is found in $M(2)$, where Fe is dominant in khomyakovite, and Mn in manganokhomyakovite.

The eudialyte structure is more or less centrosymmetric, depending on the degree of disorder and the chemical content of certain sites. The classic eudialyte *sensu stricto* is rich in Si, Fe and Ca, and represents the most centrosymmetric structure. As substitutions of the type Si ⇒ (Nb,W), Fe ⇒ Mn, (Ca,Na) ⇒ (*REE*,Sr) take place, the structures depart progressively from centrosymmetry (Johnsen & Grice 1999). Khomyakovite is a distinctly acentric eudialyte-group mineral, as demonstrated by the low $|E^2 - 1|$ value (Table 2). This departure from centrosymmetry is largely due to the significant difference in the chemical content of the two pairs of pseudosymmetrical sites $M(3)$ *versus* $Si(7)$ and $Na(4)$ *versus* $Na(3)$. In $M(3)$, 51.28 *epfu* (electrons per formula unit) are found *versus* 14.62 *epfu* in $Si(7)$, and

103.02 *epfu* in *Na*(4) *versus* 45.10 *epfu* in *Na*(3). Compared with corresponding data for other eudialyte-group samples investigated by Johnsen & Grice (1999), khomyakovite has the highest scattering power at *M*(3) as well as at *Na*(4) observed thus far. It is further characterized by being one of the very few eudialyte-group phases with Fe mostly five-fold-coordinated in *M*(2) and by being among the relatively few samples with *M*(2) [*M*(2,4) and *M*(2,5) together, *i.e.,* *M*(2) both in four-fold and in five-fold coordination (Johnsen & Grice 1999)] close to being fully occupied. Bond-valence calculations indicate that the Fe is divalent.

For manganokhomyakovite, for which no single-crystal data are available, the similarity in chemical composition, except for the Fe:Mn ratio, strongly suggests a similar degree of departure from centrosymmetry; therefore, this species is assigned to space group *R3m* as well.

REFERENCES

HORVÁTH, L. & GAULT, R.A. (1990): The mineralogy of Mont St. Hilaire, Quebec. *Mineral. Rec.* **21**, 284-360.

JOHNSEN, O. & GAULT, R.A. (1997): Chemical variation in eudialyte. *Neues Jahrb. Mineral., Abh.* **171**, 215-237.

_____ & GRICE, J.D. (1999): The crystal chemistry of the eudialyte group. *Can. Mineral.* **37**, 865-891.

_____, _____ & GAULT, R.A. (1998): Kentbrooksite from the Kangerdlugssuaq intrusion, East Greenland, a new Mn–REE–Nb–F end-member in a series within the eudialyte group: description and crystal structure. *Eur. J. Mineral.* 10, 207-219.

_____, _____ & _____ (1999): Oneillite: a new Ca-deficient and REE-rich member of the eudialyte group from Mont Saint-Hilaire, Quebec, Canada. *Can. Mineral.* **37** (in press).

MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

NORTH, A.T.C., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.

SHELDRICK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package* (revision 4.1). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin.

_____ (1993): *SHELXL-93. Program for the Refinement of Crystal Structures.* University of Göttingen, Göttingen, Germany.