

JOHNSENITE-(Ce): A NEW MEMBER OF THE EUDIALYTE GROUP FROM MONT SAINT-HILAIRE, QUEBEC, CANADA

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ABSTRACT

Johnsenite-(Ce), ideally $\text{Na}_{12}(\text{Ce},\text{La},\text{Sr},\text{Ca},\square)_3\text{Ca}_6\text{Mn}_3\text{Zr}_3\text{W}(\text{Si}_{25}\text{O}_{73})(\text{CO}_3)(\text{OH},\text{Cl})_2$, is a new member of the eudialyte group from Mont Saint-Hilaire, Quebec, and is the W analogue of zirsilite-(Ce). It occurs as deeply etched, skeletal crystals to 4 mm and aggregates of crystals to 1 cm. Associated minerals include, albite, calcite, pectolite, aegirine, fluorapophyllite, zirsilite-(Ce), a burbankite-group phase, dawsonite, rhodochrosite, epididymite, galena, molybdenite, pyrite, pyrrhotite, quartz, an amphibole-group mineral, sphalerite, stillwellite-(Ce), titanite, cerite-(Ce), tuperssuatsiaite, steacyite, catapleite, zakharovite, natrolite and microcline. It is transparent to translucent with a vitreous luster and white streak. It is brittle with a Mohs hardness of 5–6. It has no discernable cleavage or parting and an uneven fracture. It is uniaxial negative with ω 1.648(1) and ϵ 1.637(1). It is trigonal, space group $R\bar{3}m$, a 14.237(3) and c 30.03(1) Å, V 5271(2) Å³, Z = 3. The eight strongest X-ray powder-diffraction lines, measured for johnsenite-(Ce) [d in Å (hkl)] are: 11.308(95)(101), 9.460(81)(012), 4.295(34)(205), 3.547(36)(220), 3.395(38)(131), 3.167(75)(217), 2.968(100)(315) and 2.849(81)(404). The infrared spectrum of johnsenite-(Ce) is given. An average result of eight electron-microprobe analyses, including three on the grain used for the structure determination, gave Na₂O 10.47, K₂O 0.25, CaO 8.98, SrO 1.60 MnO 5.43, FeO 1.61, Y₂O₃ 0.70, La₂O₃ 1.56, Ce₂O₃ 3.01, Pr₂O₃ 1.14, Nd₂O₃ 0.89, Sm₂O₃ 0.12, Gd₂O₃ 0.33, Dy₂O₃ 0.14, TiO₂ 0.73, ZrO₂ 9.60, HfO₂ 0.04, Nb₂O₅ 0.82, WO₃ 5.23, SiO₂ 43.16, Cl 0.77, CO₂ (1.27), H₂O (0.32), O = Cl –0.17, total 97.99 wt. %. Concentrations of CO₂ and H₂O were calculated by stoichiometry based on results from the crystal-structure analysis. The empirical formula of johnsenite-(Ce), based on 29 (Si⁴⁺, Zr⁴⁺, Ti⁴⁺, Hf⁴⁺, Nb⁵⁺, W⁶⁺) cations and 1 (CO₃) as determined in the crystal-structure analysis, is: Na_{11.74} [(Ce_{0.64}La_{0.33}Dy_{0.03}]_{Σ1.00}Sr_{0.54}Ca_{0.51}Y_{0.22}K_{0.19}]_{Σ2.46} (Ca_{5.06}[Pr_{0.24}Nd_{0.18}Gd_{0.06}Sm_{0.02}]_{Σ0.50}Mn_{0.44}]_{Σ6} (Mn_{2.22}Fe_{0.78}]_{Σ3} (Zr_{2.71}Ti_{0.32}Hf_{0.01}]_{Σ3.04} (W_{0.78}Nb_{0.21}]_{Σ0.99}Si_{24.97}O₇₃ (CO₃) (OH,Cl_{0.75}]_{Σ2}. $D_{\text{meas.}}$ = 3.24(3) g/cm³; $D_{\text{calc.}}$ = 3.23 g/cm³. The structure consists of four layers. The layering is distinctly polar, as indicated by the X-ray-diffraction intensity statistics, layer composition and electrostatic potential of individual crystals. The new species is named after Ole Johnsen, of the Geological Museum, University of Copenhagen, Denmark.

Keywords: johnsenite-(Ce), eudialyte, new mineral species, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La johnsenite-(Ce), de composition idéale $\text{Na}_{12}(\text{Ce},\text{La},\text{Sr},\text{Ca},\square)_3\text{Ca}_6\text{Mn}_3\text{Zr}_3\text{W}(\text{Si}_{25}\text{O}_{73})(\text{CO}_3)(\text{OH},\text{Cl})_2$, est un nouveau membre du groupe de l'eudialyte, découvert au mont Saint-Hilaire, Québec; il s'agit de l'analogue tungsténifère de la zirsilite-(Ce). Elle se présente en cristaux squelettiques fortement corrodés atteignant 4 mm, et 1 cm en agrégats. Lui sont associés albite, calcite, pectolite, aegirine, fluorapophyllite, zirsilite-(Ce), un minéral du groupe de la burbankite, dawsonite, rhodochrosite, epididymite, galène, molybdénite, pyrite, pyrrhotite, quartz, une amphibole, sphalérite, stillwellite-(Ce), titanite, cériite-(Ce), tuperssuatsiaïte, steacyite, catapléïte, zakharovite, natrolite et microcline. Elle est transparente à translucide, avec un éclat vitreux et une rayure blanche. Elle est cassante, avec une dureté de Mohs de 5 à 6. Il n'y a aucun clivage ou plan de séparation visible, et la fracture est inégale. Le minéral est uniaxe négatif, avec ω 1.648(1) et ϵ 1.637(1). Sa symétrie est trigonale, groupe d'espace $R\bar{3}m$, a 14.237(3) et c 30.03(1) Å, V 5271(2) Å³, Z = 3. Les huit raies les plus intenses du spectre de diffraction X (méthode des poudres) [d en Å (hkl)] sont: 11.308(95)(101), 9.460(81)(012), 4.295(34)(205), 3.547(36)(220), 3.395(38)(131), 3.167(75)(217), 2.968(100)(315) et 2.849(81)(404). Nous présentons le spectre infrarouge de la johnsenite-(Ce). Les résultats de huit analyses à la microsonde électronique, dont trois sur le cristal ayant servi à l'ébauche de la structure, ont donné, en moyenne, Na₂O 10.47, K₂O 0.25, CaO 8.98, SrO 1.60 MnO 5.43, FeO 1.61, Y₂O₃ 0.70, La₂O₃ 1.56, Ce₂O₃ 3.01, Pr₂O₃ 1.14, Nd₂O₃ 0.89, Sm₂O₃ 0.12, Gd₂O₃ 0.33, Dy₂O₃ 0.14, TiO₂ 0.73, ZrO₂ 9.60, HfO₂ 0.04, Nb₂O₅ 0.82, WO₃ 5.23, SiO₂ 43.16, Cl 0.77, CO₂ (1.27), H₂O (0.32), O = Cl –0.17, pour un total de 97.99% (poids). La concentration de CO₂ et celle de H₂O ont été calculées selon la stoechiométrie établie à partir de l'analyse de la structure. La formule empirique de la johnsenite-(Ce), fondée sur 29 atomes de (Si⁴⁺, Zr⁴⁺, Ti⁴⁺, Hf⁴⁺, Nb⁵⁺, W⁶⁺) et un groupe (CO₃), selon les résultats de l'analyse structurale, est: Na_{11.74} [(Ce_{0.64}La_{0.33}Dy_{0.03}]_{Σ1.00}Sr_{0.54}Ca_{0.51}Y_{0.22}K_{0.19}]_{Σ2.46} (Ca_{5.06}[Pr_{0.24}Nd_{0.18}Gd_{0.06}Sm_{0.02}]_{Σ0.50}Mn_{0.44}]_{Σ6} (Mn_{2.22}Fe_{0.78}]_{Σ3} (Zr_{2.71}Ti_{0.32}Hf_{0.01}]_{Σ3.04} (W_{0.78}Nb_{0.21}]_{Σ0.99}Si_{24.97}O₇₃ (CO₃) (OH,Cl_{0.75}]_{Σ2}. $D_{\text{meas.}}$ = 3.24(3) g/cm³; $D_{\text{calc.}}$ = 3.23 g/cm³. La structure est faite de

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quatre couches, qui définissent une polarité, telle qu'indiquée par une analyse statistique des intensités des pics de diffraction, la composition des couches et le potentiel électrostatique des monocristaux. Le nom du minéral honore Ole Johnsen, du Musée Géologique, Université de Copenhague, au Danemark.

(Traduit par la Rédaction)

Mots-clés: johnsenite-(Ce), eudialyte, nouvelle espèce minérale, structure cristalline, mont Saint-Hilaire, Québec.

INTRODUCTION

Over many years, Dr. Peter Tarasoff, an avid mineral collector from Montreal, Quebec, has provided the authors with numerous samples of "eudialyte" from Mont Saint-Hilaire, Quebec, for their systematic study of the eudialyte-group minerals. On September 16, 2000, he collected the sample that is the subject of this paper. Subsequent chemical and X-ray analyses showed this sample to be a new member of the eudialyte group. Herein, we present the data that establish it as a new species, johnsenite-(Ce). It is interesting to note that during the course of the investigation, another species of eudialyte, zirsilite-(Ce), the Nb analogue of johnsenite-(Ce), was identified from the same material. We have not been able to distinguish these two species from one another except by structural or chemical analysis, as discussed later in this paper. It perhaps should be restated here that in describing a new eudialyte-group species, a crystal-structure analysis is essential (Johnsen *et al.* 2003a). However for routine identification of eudialyte-group minerals, a chemical analysis is generally sufficient, using the method recommended by Johnsen & Grice (1999).

Johnsenite-(Ce) is named in honor of Ole Johnsen (b. 1940), Geological Museum, University of Copenhagen, Denmark for his extensive research into the eudialyte group and for his contributions to mineralogy in general, both scientific and popular. In particular, his research has focused on the mineralogy of Greenland, and has involved numerous excursions to its alkaline rock and carbonatite deposits. In 2000, he completed a field guide to minerals, entitled *Minerals of the World*, which is now published in seven languages. He also is coauthor of Special Publication 8 of *The Canadian Mineralogist*, entitled "Mineral Species First Described from Greenland".

The new mineral and its name have been approved by the Commission on New Minerals and Mineral Names (CNMMN), IMA (IMA #2004-026). The name is in keeping with the recommendations of the Subcommittee on Eudialyte Nomenclature of the CNMMN (Johnsen *et al.* 2003a). One of the recommendations of the Subcommittee is that the anion site be ignored in general, in terms of the nomenclature of this group. The holotype specimen (catalogue #CMNMC 84395) is housed in the collection of the Canadian Museum of Nature, Ottawa.

OCCURRENCE

Johnsenite-(Ce) was found in the Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Quebec, an alkaline intrusive complex of Cretaceous age, approximately 40 km east of Montreal. Quarrying operations have exposed numerous pegmatites, miarolitic cavities, breccias and xenoliths in that part of the intrusion described as the East Hill Suite (Currie 1989), which consists primarily of sodalite and nepheline syenites. Johnsenite-(Ce) was collected from a zone of igneous breccia in the southeast wall of the quarry on the level 7 bench. The breccia appears to have been emplaced along a contact between porphyritic nepheline syenite and sodalite syenite, and is characterized by the presence of numerous fragments of marble, some up to a meter or more in size. Johnsenite-(Ce) was found in irregular cavities, ranging in size from a millimeter to about 6 cm across, along the margins of a large fragment of marble. It appears to have formed late in the paragenetic sequence within the cavities. It is also found as grains less than a millimeter in size, embedded in the cavity linings, typically in pectolite or albite. The principal associated minerals in the cavities are albite, calcite, pectolite, aegirine, and fluorapophyllite. Minor associated species are zirsilite-(Ce), a burbankite-group mineral, dawsonite, rhodochrosite, epididymite, galena, molybdenite, pyrite, pyrrhotite, quartz, an amphibole-group mineral, sphalerite, stillwellite-(Ce), titanite, cerite-(Ce), taperssuatsiaite, steacyite, catapleiite, zakharovite, natrolite and microcline. The complexity of the East Hill Suite is reflected in the wide variation in chemical composition of the eudialyte-group minerals found there (Johnsen & Gault 1997). In addition to johnsenite-(Ce), seven other members of the eudialyte group, namely eudialyte *sensu stricto* (*s.s.*), kentbrooksite (Johnsen *et al.* 1998), khomyakovite and manganokhomyakovite (Johnsen *et al.* 1999a), oneillite (Johnsen *et al.* 1999b), ferrokentbrooksit (Johnsen *et al.* 2003b) and zirsilite-(Ce) (Khomyakov *et al.* 2003) have been identified from Mont Saint-Hilaire during the course of our systematic examination of eudialyte-group minerals from this locality. Johnsenite-(Ce) appears to be a rare member of the eudialyte group at Mont Saint-Hilaire. Only approximately 500 mg is known to exist.

PHYSICAL AND OPTICAL PROPERTIES

Johnsenite-(Ce) occurs as pale yellow to bright orange, deeply etched, skeletal crystals to 4 mm and aggregates of crystals to 1 cm (Fig. 1). Several partial faces were observed, presumably belonging to the forms $\{0001\}$ and $\{10\bar{1}1\}$ (pers. commun., P. Tarassoff). No signs of twinning were observed. The crystals are vitreous, translucent to transparent, with a white streak. Johnsenite-(Ce) is non-fluorescent in short- and long-wave ultraviolet light. It is brittle, without discernable cleavage or parting, and has an uneven fracture. It has a Mohs hardness of 5–6. The density of johnsenite-(Ce), measured by suspension in methylene iodide, is 3.24(3) g/cm³, comparing well with the calculated density of 3.23 g/cm³.

Johnsenite-(Ce) is uniaxial negative, $\omega = 1.648(1)$ and $\varepsilon = 1.637(1)$ ($\lambda = 589$ nm). These optical parameters were determined on a single grain that had been previously analyzed to assure that the chemical composition was that of johnsenite-(Ce). In transmitted light, thin grains appear colorless. The mineral

shows no pleochroism. A Gladstone–Dale calculation gives a compatibility index of 0.014, which is rated as superior (Mandarino 1981). Like other non-centrosymmetric members of the eudialyte group, johnsenite-(Ce) displays an active static electric repulsion when approached by a steel needle. This electrical property is reminiscent of the behavior of members of the tourmaline group.

CHEMICAL COMPOSITION

Chemical analyses were done in wavelength-dispersion 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 accelerating voltage was 15 kV, and the beam current was 20 nA. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first, except that for the lanthanides and hafnium, which were collected for 100 s. Most grains analyzed from the holotype specimen correspond to johnsenite-(Ce) in



FIG. 1. An aggregate of johnsenite-(Ce) crystals on matrix. The aggregate measures 10 × 7 mm. Associated species are: calcite (transparent), aegirine (dark green) and microcline (white). P. Tarassoff specimen. Photo by L. Horváth.

composition; other grains from the same sample gave a zirsilite-(Ce) composition (Table 1), however. We used the following standards in the electron-microprobe analyses: albite (NaK α), almandine (SiK α , FeK α), zircon (ZrL α), sanidine (KK α), gehlenite (CaK α), rutile (TiK α), celestine (SrL α), tephroite (MnK α), a set of synthetic REE phosphates (LaL α , CeL α , PrL β , NdL α , SmL α , GdL α , DyL α), synthetic yttrium iron garnet (YL α), synthetic hafnon (HfL α), synthetic MnNb₂O₆ (NbL α), synthetic CoWO₄ (WL α) and meionite (ClK α). The following elements were sought but not detected: F, Mg, Al, Zn, Rb, Cs, Ba, Eu, Tb, Ho, Er, Tm, Yb, Lu, Ta and Th. Data for elements in the standards were collected for 50 s or 0.25% precision, whichever was attained first. The presence of CO₂ and H₂O was confirmed in johnsenite-(Ce) by infrared spectroscopy and crystal-structure analysis. An average result of eight analyses, performed on four grains from the holotype specimen of johnsenite-(Ce), including three performed

on the grain chosen for structure analysis (with ranges) (Table 1, column 1), was used to determine the following empirical formula of johnsenite-(Ce), based on 29 (Si⁴⁺, Zr⁴⁺, Ti⁴⁺, Hf⁴⁺, Nb⁵⁺, W⁶⁺) cations and one (CO₃) group as determined from the crystal-structure analysis: Na_{11.74}([Ce_{0.64}La_{0.33}Dy_{0.03}]_{Σ1.00} Sr_{0.54}Ca_{0.51}Y_{0.22}K_{0.19}Hf_{0.01}]_{Σ2.47} (Ca_{5.06}[Pr_{0.24}Nd_{0.18}Gd_{0.06}Sm_{0.02}]_{Σ0.50}Mn_{0.44})]_{Σ6}(Mn_{2.22}Fe_{0.78})]_{Σ3}(Zr_{2.71}Ti_{0.32})]_{Σ3.03}(W_{0.78}Nb_{0.21})]_{Σ0.99}Si_{24.97}O₇₃(CO₃)(OH, Cl_{0.75})]_{Σ2} or, ideally, Na₁₂(Ce,La,Sr,Ca,□)₃Ca₆Mn₃WSiZr₃(Si₂₄O₇₂)O(CO₃)(OH,Cl)₂. This formula is in keeping with the general formula proposed by Johnsen *et al.* (2003a): Na₁₂[N(4)]₃ [M(1)]₆[M(2)]₃ [M(3)] [M(4)]Zr₃(Si₂₄O₇₂)O[•]₄X₂, X = Cl, F, OH, or CO₃; Z = 3. In this formula, Na₁₂ is a condensation of N(1)₃N(2)₃N(3)₃N(5)₃. A more conventional way to write this formula for easy comparison to other members of the eudialyte group in the literature is: Na₁₂(Ce,La,Sr,Ca,□)₃Ca₆Mn₃Zr₃W(Si₂₅O₇₃)(CO₃)

TABLE 1. CHEMICAL COMPOSITION OF JOHNSENITE-(Ce) AND ZIRSIILITE-(Ce) FROM MONT SAINT-HILAIRE, QUEBEC

	Chemical composition (wt.%)					atoms per formula unit (<i>apfu</i>)			
	1	2	3	4		1	2	3	4
Na ₂ O	10.47 (10.29-10.72)	10.55	10.05	10.70	Na	11.74	11.84	11.24	11.96
K ₂ O	0.25 (0.23-0.30)	0.26	0.22	0.30	K	0.19	0.19	0.17	0.22
CaO	8.98 (8.18-9.58)	9.32	7.90	7.47	Ca	5.57	5.78	4.88	4.61
SrO	1.60 (0.84-2.15)	1.91	1.54	0.89	Sr	0.54	0.64	0.51	0.30
MnO	5.43 (4.96-6.13)	5.18	7.23	7.67	Mn ²⁺	2.66	2.54	3.53	3.75
FeO	1.61 (1.34-1.85)	1.71	1.18	0.62	Fe ³⁺	0.78	0.83	0.57	0.30
Al ₂ O ₃	0.00*	0.00	0.23	0.00	Al	0.00	0.00	0.16	0.00
Y ₂ O ₃	0.70 (0.57-0.93)	0.61	1.12	1.59	Y	0.22	0.19	0.34	0.49
La ₂ O ₃	1.56 (1.38-1.80)	1.48	1.61	1.11	La	0.33	0.32	0.34	0.24
Ce ₂ O ₃	3.01 (2.53-3.82)	2.70	3.70	3.01	Ce	0.64	0.57	0.78	0.63
Pr ₂ O ₃	1.14 (0.81-1.48)	0.97	1.26	1.24	Pr	0.24	0.21	0.27	0.26
Nd ₂ O ₃	0.89 (0.60-1.57)	0.68	0.94	1.05	Nd	0.18	0.14	0.19	0.22
Sm ₂ O ₃	0.12 (0.00-0.32)	0.00	0.37	0.00	Sm	0.02	0.00	0.07	0.00
Gd ₂ O ₃	0.33 (0.25-0.42)	0.26	0.12	0.41	Gd	0.06	0.05	0.02	0.08
Dy ₂ O ₃	0.14 (0.00-1.12)	0.00	0.00	0.44	Dy	0.03	0.00	0.00	0.08
TiO ₂	0.73 (0.60-0.84)	0.71	0.79	0.47	Ti	0.32	0.31	0.34	0.20
ZrO ₂	9.60 (9.44-9.85)	9.72	9.11	9.62	Zr	2.71	2.74	2.56	2.70
HfO ₂	0.04 (0.00-0.12)	0.04	0.12	0.14	Hf	0.01	0.01	0.02	0.02
Nb ₂ O ₅	0.82 (0.59-1.22)	0.60	1.28	1.61	Nb	0.21	0.16	0.33	0.42
Ta ₂ O ₅	0.00	0.00	0.09	0.23	Ta	0.00	0.00	0.01	0.04
WO ₃	5.23 (4.48-5.67)	5.47	2.31	1.02	W	0.78	0.82	0.35	0.15
SiO ₂	43.16 (42.80-43.54)	43.12	43.74	44.17	Si	24.97	24.96	25.23	25.46
CO ₂ **	1.27	1.27	1.26	1.27	C	1	1	1	1
Cl	0.77 (0.70-0.84)	0.82	0.68	0.54	Cl	0.75	0.81	0.66	0.53
H ₂ O***	0.32	0.31	0.34	0.38	H	1.25	1.19	1.33	1.47
O=Cl	-0.17	-0.19	-0.15	-0.12	O	79.2	79.1	79.4	78.9
Total	97.99	97.50	97.04	95.83					

* 0.00 denotes an analytical result that is less than the detection limit. For any number greater than 0.00, the element has been detected.

** calculated from the crystal-structure analysis. *** calculated such that Cl + OH = 2 in site X.

Columns: 1: Johnsenite-(Ce), average result of eight analyses (with ranges) on four grains. 2: Johnsenite-(Ce), average result of three analyses of the grain used for the structure determination. 3: Zirsilite-(Ce) or johnsenite-(Ce); composition of crystal #2. 4: Zirsilite-(Ce); composition of crystal #3.

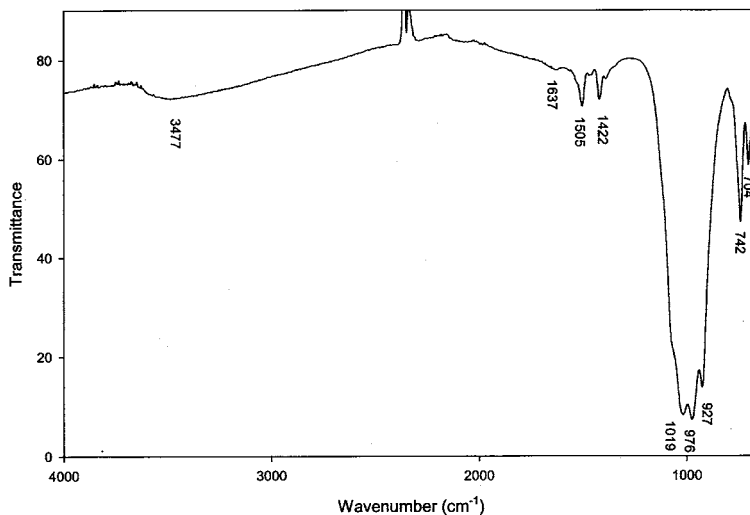


FIG. 2. Infrared spectrum of johnsenite-(Ce).

(OH,Cl)₂. The grouping of the REE at the *N*(4) site, rather than just listing all of the elements according to their abundance in the chemical analysis, emphasizes the use of Levinson modifiers in the naming of minerals (Nickel & Grice 1998).

Johnsenite-(Ce) is closely related chemically to zirsilite-(Ce), in which *M*(4) is occupied by Nb rather than W, and to manganokhomyakovite, in which *N*(4) is occupied by Sr rather than the REE. An electron-microprobe analysis suffices to differentiate these three species.

INFRARED ANALYSIS

For analysis by Fourier transform infrared (FTIR) spectroscopy, a grain from the sample was positioned on a diamond anvil microsample cell and analyzed using a Spectra-Tech IR-Plan research microscope interfaced to a Bomem Michelson MB-120 spectrometer. Two hundred scans were collected over the range 4000–660 cm⁻¹ (Fig. 2). The broad absorption bands (cm⁻¹) at 3477 and 1637 are assigned to the [OH] stretching mode and the [H₂O] bending mode, respectively. The two small bands at 1505 and 1422 are attributed to the stretching mode of a [CO₃] group. These bands are also present in kentbrooksitite (Johnsen *et al.* 1998), manganokhomyakovite (Johnsen *et al.* 1999a) and oneillite (Johnsen *et al.* 1999b). The presence of (CO₃) in the eudialyte structure was discussed by Johnsen *et al.* (1999b). In a well-ordered structure, a single [CO₃] group on a 3-fold axis would have only one band in the 1600–1300 region. The observed splitting can be attributed to disorder within the [CO₃] group or to the pres-

ence of another [CO₃] group or portion thereof in the *X* site. The bands at 1019, 976 and 927 are assigned to the symmetric stretching of [SiO₄] and indicate considerable splitting of the [SiO₄] vibration modes, attributable to a structure with more than one crystallographically distinct [SiO₄] group. Bands at 742 and 704 are assigned to bending of [SiO₄]. A digital version of the spectrum is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray powder-diffraction data obtained with a Bruker micro-diffractometer equipped with a 2-D grid detector, a crystal-to-detector distance of 6 cm, using CuK α radiation, are given in Table 2. The instrument was calibrated with synthetic corundum. Indexing of the powder data was aided with powder-pattern intensities calculated from the crystal-structure analysis.

Of the four single-crystal data collections, one is for a borderline case of zirsilite-(Ce) – johnsenite-(Ce) (Table 1, column 3), one is for zirsilite-(Ce) (Table 1, column 4), and two are for johnsenite-(Ce) (Table 1, column 2). It is of interest that the zirsilite-(Ce) specimens were initially identified by crystal-structure analysis on the basis of site-occupancy factors and later verified by electron-microprobe analyses. This confirms the strength of the structure-analysis technique for refining the number of electrons to such accuracy as to define the chemical contents. All of the eudialyte-group crystals were chosen from the same small

sample. Initially, we did not realize that there were two species, johnsenite-(Ce) and zirsilite-(Ce) present, as their physical properties are identical. Once this was known, the johnsenite-(Ce) crystals were removed from an analyzed electron-microprobe mount, ground into spheres, and the intensity data collected. Neither of the johnsenite-(Ce) crystals gave as good a refinement as the zirsilite-(Ce) crystals because the rather brutal treatment of making a polished mount and then digging the crystal back out inevitably fractures this brittle mineral. The better-quality one of the two refinements is presented here. A ground sphere of johnsenite-(Ce), 200 μm in diameter, was mounted on a CCD-equipped Bruker P4 fully automated four-circle diffractometer operated at 50 kV and 40 mA. In excess of a hemisphere of intensity data was collected out to $2\theta = 60^\circ$ using a 20 s frame time, a frame width of 0.2° and a crystal-to-detector distance of 4 cm. With these operating conditions, no decrepitation was evident in the final analysis of the intensity standards. Information relevant to the data collection and structure determination is given in Table 3. The three-dimensional data were reduced for Lorentz, polarization, and background effects using the Bruker program SAINT and an empirical absorption correction using SADABS (Sheldrick 1998).

The crystal-structure refinement was done with the *SHELX-97* program (Sheldrick 1997). Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.723, indicating a non-centrosymmetric space-group. The $|E^2 - 1|$ value is significantly

lower than for other samples of the eudialyte group, which have values in the range 0.70 to 1.04 (Johnsen & Grice 1999). The incongruously low value of $|E^2 - 1|$ for johnsenite-(Ce) is a result of merohedral twinning (Herbst-Irmer & Sheldrick 1998). After the introduction of the twin operator, the *R* index for all data dropped from 0.072 to 0.045. The strategy applied to the final stages of the refinement, as well as the site-assignment procedure, are described in detail by Johnsen & Grice (1999). Lowering the symmetry to space group *R3*, as in the oneillite structure (Johnsen *et al.* 1999b), did not improve the model, as there is no indication of order at the *M*(1) site. The final coordinates and displacement parameters of the atoms are shown in Table 4, selected bond-lengths in Table 5. Table 6 shows selected site-scattering values (*epfu*) and site populations (*apfu*) pertinent to the crystal used in the structure refinement. A listing of observed and calculated structure-factors has been submitted to CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Johnsenite-(Ce) is a member of the eudialyte group, which now numbers a total of 18 species (Johnsen *et al.* 2003). The crystal structure is complex; it has a large number of atomic sites, many of which are split or disordered, and several of which may have vacancies. This leads to the problem that neither the number of cations nor of anions is fixed. As described by Johnsen & Grice (1999), the crystal structure of eudialyte-group minerals consists of layers on [001] (Fig. 3). For most species in the group, the *c* dimension is $\sim 30 \text{ \AA}$ if referred to hexagonal axes. The four fundamental layers, labeled A, B, C, and D in Figure 4, define the building units in the non-centrosymmetric, singly-primitive rhombohedral cell. These four layers are tripled by rhombohedral lattice centering in the transformed hexagonal lattice, making a total of 12 layers in the triply primitive hexagonal unit-cell, in space group *R3m*. Except for oneillite (Johnsen *et al.* 1999b), which crystallizes in space group *R3*, all other species of eudialyte belong to either *R3m* or *R3m* space groups. For the centrosymmetric space-group, *R3m*, only three layers are required to describe the structure, as the silica layers (layers B and D) are crystallographically identical owing to the presence of a center of symmetry at height one-sixth.

In johnsenite-(Ce), layer A consists of Na atoms in large Na(1) and Na(2) polyhedra cross-linked by Zr in octahedral coordination. Layer C consists of six-membered rings of $[\text{Ca}(1)\text{O}_6]$ octahedra joined by $[\text{MnO}_n]$ polyhedra and sandwiched between two pseudo-centrosymmetrically related layers of three- and nine-membered silicate rings. These ring-silicate layers differ significantly from one another in johnsenite-(Ce), which eliminates the center of symmetry. There are differences between layer B and layer D. Layer B has centering of

TABLE 2. JOHNSENITE-(Ce): X-RAY POWDER-DIFFRACTION DATA

<i>l</i> _{obs}	<i>l</i> _{calc} *	<i>d</i> _{obs}	<i>d</i> _{calc} **	<i>h</i>	<i>k</i>	<i>l</i>	<i>l</i> _{obs}	<i>l</i> _{calc} *	<i>d</i> _{obs}	<i>d</i> _{calc} **	<i>h</i>	<i>k</i>	<i>l</i>
95	100	11.299	11.406	1	0	1	6	13	2.323	2.323	2	4	1
30	20	10.055	10.011	0	0	3	21	19	2.133	2.134	3	1	11
81	65	9.452	9.529	0	1	2				2.124	5	1	4
25	23	6.440	6.413	1	0	4	4	7	2.056	2.059	3	2	10
21	28	6.048	6.039	0	2	1	10	18	1.9785	1.9797	4	2	8
24	22	5.717	5.703	2	0	2	9	5	1.9725	1.9743	5	2	0
34	20	4.291	4.302	2	0	5	6	5	1.9676	1.9678	5	1	7
30	25	4.107	4.110	3	0	0				1.9010	6	0	6
25	26	3.961	3.959	2	1	4	5	10	1.9001	1.8327	4	3	7
20	15	3.800	3.802	3	0	3				1.8325	4	1	12
36	44	3.544	3.556	2	2	0	15	13	1.8317	1.7823	5	1	10
38	47	3.392	3.398	1	3	1	31	31	1.7799	1.7796	4	4	0
32	10	3.360	3.354	2	2	3	11	12	1.7614	1.7608	0	4	14
22	10	3.342	3.337	0	0	9	5	5	1.7155	1.7148	7	0	4
75	45	3.164	3.156	2	1	7	7	12	1.6781	1.6768	4	4	6
100	90	2.966	2.972	3	1	5	6	15	1.6022	1.6032	4	0	16
81	75	2.847	2.851	4	0	4	6	9	1.5942	1.5946	0	7	8
11	7	2.685	2.691	4	1	0	6	4	1.5466	1.5449	5	4	4
10	14	2.648	2.647	3	1	6	6	5	1.5426	1.5408	1	5	14
20	30	2.593	2.591	3	0	9	6	5	1.5393	1.5392	0	8	1
4	3	2.563	2.559	2	3	5	3	4	1.5333	1.5331	8	0	2
							7	10	1.4797	1.4801	0	7	11
11	12	2.523	2.524	2	1	10	4	5	1.4032	1.4031	1	8	5
							6	8	1.3688	1.3694	5	5	6
17	19	2.370	2.370	4	1	6	4	4	1.3461	1.3453	8	2	0
							3	2	1.3414	1.3421	8	0	11

* calculated from the crystal structure using XPOW (Sheldrick 1977)

** calculated *d*-values based on refined cell parameters: *a* 14.237(3), *c* 30.03(1) Å.

the nine-membered ring by $[M(4)O_4]$ tetrahedra, where $M(4)$ is largely Si; centering of the other triad axis by a $[CO_3]$ group crosslinks the trimer of $[N(4)O_{10}]$ polyhedra, where $N(4)$ contains REE, Sr and vacancies.

TABLE 3. JOHNSENITE-(Ce): DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Simplified formula	$Na_{12}(Ce,La,SrCa,\square)_3Ca_6Mn_3Zr_3W(Si_{25}O_{73})(CO_3)(OH,Cl)_2$
Space group: $R\bar{3}m$	Reflections collected 13,953
Radiation: MoK α	Unique reflections 3,490
Graphite monochromator	Observed reflections ($> 4\sigma F_o$) 1,925
a 14.2675(7) Å	$R(int) = 0.0354$
c 30.0369(14) Å	$ E^2 - 1 = 0.723$
V 5295.2(7) Å ³	Goof = 1.157 (all data)
$Z = 3$	μ 3.06 mm ⁻¹
$R = \Sigma(F_o - F_c) / \Sigma F_o = 0.040$ (for unique F_o), 0.044 (for all F_o), 0.045 (for all F)	
Crystal size (sphere diameter) 0.20 mm	
$wR^2 = [\Sigma w(F_o - F_c)^2] / \Sigma w(F_o)^2 = 0.105$	
$w = 1/[\sigma^2 F_o^2 + (0.059 \times P)^2 + 43.2 \times P]P = (\text{Max}(F_o^2, 0) + 2 F_o^2)/3^2 + 2$	

Layer D has the $[WO_6]$ octahedron centering the nine-membered ring, and the other triad axis has a Cl atom that crosslinks trimers of $[Na(3)O_7Cl]$ polyhedra.

Johnsen & Grice (1999) compiled an interesting set of relationships between the statistic $|E^2 - 1|$ and three different parameters: (1) density, (2) REE contents, and (3) the $M(3) : M(3) + M(4)$ site-content ratio. In plots of all three of these variable parameters, there is a strong, negative correlation with $|E^2 - 1|$, which increases from 0.70 to 1.05. As the eudialyte-group mineral increasingly departs from non-centrosymmetry, therefore, each of these variables increases. Johnsenite-(Ce) would plot nearest to the end of maximum non-centrosymmetry ($|E^2 - 1| = 0.723$), close to oneillite ($|E^2 - 1| = 0.702$) (Johnsen *et al* 1999b). Thus these are highly polar crystals. As discussed above, the degree to which a eudialyte species is non-centrosymmetric depends on the disparity of polyhedral sites $M(3)$ versus $M(4)$ and $N(3)$ versus $N(4)$. Both johnsenite-(Ce) and oneillite contain

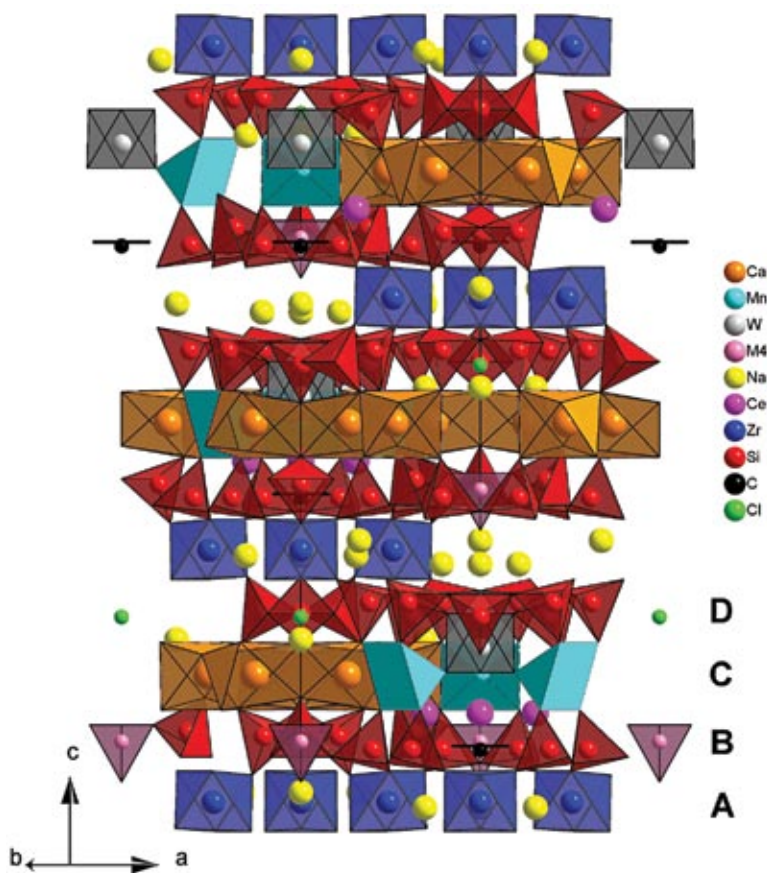


Fig. 3. Contents of one unit cell for johnsenite-(Ce). There are 12 layers stacked along (001), of which there are four fundamental layers (A, B, C, D) that are repeated through the rhombohedral centering. The horizontal (CO_3) group appears as a thick black line.

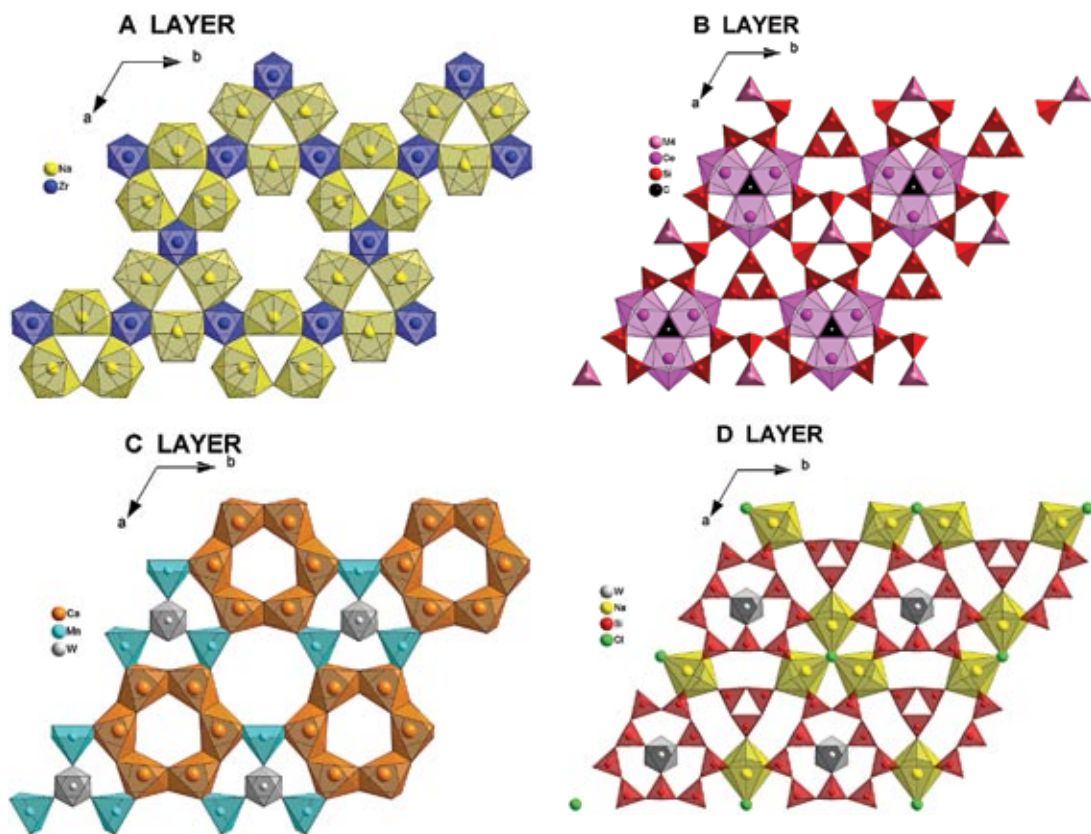


FIG. 4. The four fundamental layers of the johnsenite-(Ce) crystal structure: (A) $[\text{ZrO}_6]$ and $[\text{Na}(1a)\text{O}_9]$ polyhedra; (B) three- and nine-membered rings of $[\text{SiO}_4]$ tetrahedra centered by $[\text{Si}(4)\text{O}_4]$ tetrahedra and cross-linked by $[\text{Ce}(4)\text{O}_{10}]$ and $[\text{CO}_3]$ polyhedra; (C) six-membered rings of $[\text{CaO}_6]$ octahedra cross-linked by trimers of $[\text{Mn}(2,5)\text{O}_5]$ tetragonal pyramids centered by $[\text{W}(3)\text{O}_6]$ octahedra; (D) three- and nine-membered rings of $[\text{SiO}_4]$ tetrahedra centered by $[\text{W}(3)\text{O}_6]$ octahedra and cross-linked by trimers of $[\text{Na}(3)\text{O}_7\text{Cl}]$ polyhedra.

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TABLE 5. JOHNSENITE-(Ce): SELECTED INTERATOMIC DISTANCES (Å)

Ca(1)–O(2)	2.270(2)	Si(1)–O(2)	1.587(4)	Na(1a)–O(16)	2.518(4) × 2	Na(3)–O(17)	2.520(2) × 2
Ca(1)–O(17)	2.326(3)	Si(1)–O(3)	1.600(4)	Na(1a)–O(6)	2.577(3) × 2	Na(3)–O(11)	2.659(5)
Ca(1)–O(5)	2.334(2)	Si(1)–O(1)	1.646(2) × 2	Na(1a)–O(18)	2.687(6)	Na(3)–Cl(2a)	2.69(2)
Ca(1)–O(11)	2.356(2)			Na(1a)–O(4)	2.704(6)	Na(3)–Cl(2b)	2.767(6)
Ca(1)–O(14)	2.363(2)	Si(2)–O(5)	1.591(4)	Na(1a)–O(10)	2.846(5) × 2	Na(3)–O(16)	2.842(4) × 2
Ca(1)–O(8)	2.447(2)	Si(2)–O(6)	1.615(4)	Na(1a)–Na(1b)	0.870(8)	Na(3)–O(2)	2.996(5)
		Si(2)–O(4)	1.647(2) × 2			Na(3)–O(2)	3.096(11)
Mn(2,5)–O(17)	2.136(2) × 2			Na(1b)–O(16)	2.395(4) × 2		
Mn(2,5)–O(14)	2.143(2) × 2	Si(3)–O(9)	1.604(4)	Na(1b)–O(6)	2.413(3) × 2	Ce(4)–O(14)	2.477(3) × 2
Mn(2,5)–O(19)	2.182(4)	Si(3)–O(8)	1.611(3)	Na(1b)–O(18)	2.930(7)	Ce(4)–O(1b)	2.551(3) × 2
Mn(2,5)–M(2,4)	0.64(1)	Si(3)–O(7)	1.643(3) × 2	Na(1b)–O(4)	2.964(8)	Ce(4)–O(8)	2.600(4)
				Na(1b)–Cl(2b)	3.039(12)	Ce(4)–O(19)	2.739(3) × 2
Mn(2,4)–O(17)	2.060(10) × 2	Si(4)–O(11)	1.568(4)			Ce(4)–O(13)	2.825(3) × 2
Mn(2,4)–O(14)	2.189(10) × 2	Si(4)–O(12)	1.602(5)	Na(2)–O(15)	2.452(4)	Ce(4)–O(5)	2.827(4)
		Si(4)–O(10)	1.640(3) × 2	Na(2)–O(1)	2.516(5)		
W(3)–O(19)	1.837(4) × 3			Na(2)–O(3)	2.639(3) × 2	Na(5)–O(20)	2.225(6)
W(3)–O(9)	2.049(4) × 3	Si(5)–O(16)	1.599(3)	Na(2)–O(13)	2.767(7) × 2	Na(5)–O(18)	2.265(5)
		Si(5)–O(17)	1.603(3)	Na(2)–X(1b)	2.767(3)	Na(5)–O(9)	2.583(5) × 2
Si(4*)–O(12)	1.603(5) × 3	Si(5)–O(18)	1.661(2) × 2	Na(2)–O(7)	2.874(3) × 2		
Si(4*)–O(20)	1.612(9)					Zr–O(3)	2.049(3)
		Si(6)–O(13)	1.589(2)			Zr–O(16)	2.058(3) × 2
		Si(6)–O(14)	1.618(2)			Zr–O(13)	2.060(2) × 2
		Si(6)–O(10)	1.638(1)			Zr–O(6)	2.080(4)
		Si(6)–O(15)	1.637(1)				
						C(1a)–O(1b)	1.277(5) × 3

TABLE 6. JOHNSENITE-(Ce): SITE-SCATTERING FACTORS (*epfu*) AND SITE POPULATIONS (*apfu*)

<i>site</i>	<i>sfac</i>	<i>sof</i>	<i>M/3</i> **	<i>epfu</i> (X-ray refined)	<i>apfu</i> (assigned)***	<i>epfu</i> (EMPA)
<i>M</i> (1)	Ca	1.181(2)	6	142	5.23Ca + 0.40REE + 0.367Mn	137
<i>M</i> (2,5)	Mn	0.446(1)	3	66.9 + <i>M</i> (24) = 72.9	2.17Mn + 0.83Fe	75.8
<i>M</i> (2,4)	Mn	0.040(1)	3	5.96		
<i>M</i> (3)	W	0.120(3)	1	53.2 + 11.3 = 64.5	0.82W + 0.16Nb	67.2
<i>M</i> (3)	Nb	0.046(3)	1	11.3		
<i>M</i> (4)	Si	0.134(1)	1	11.2	0.96Si	13.4
<i>N</i> (1a)	Na	0.327(4)	3	21.6 + <i>N</i> (1b) + <i>N</i> (2) + <i>N</i> (3) + <i>N</i> (5) = 129	2.90Na	130
<i>N</i> (1b)	Na	0.186(3)	3	12.3		
<i>N</i> (2)	Na	0.5	3	33	3Na	
<i>N</i> (3)	Na	0.5	3	33	3Na	
<i>N</i> (4)	Y*	0.4388(7)	3	103	1.08REE + 0.64Sr + 0.19K + 0.55Ca	104
<i>N</i> (5)	Na	0.464(4)	3	30.6		
<i>Z</i>	Zr	0.4728(6)	3	113	2.74Zr + 0.31Ti + 0.01Hf	117
<i>O</i> (20)	O	0.140(3)	1	6.75		
<i>X</i> (1a)	C	0.257(5)	1			
<i>X</i> (1b)	O	0.341(5)	3	16.4		
<i>X</i> (2a)	Cl	0.088(3)	1	9.03 + <i>X</i> (2b) = 14.1	0.75Cl	12.8 + OH
<i>X</i> (2b)	Cl	0.050(2)	1	5.07		

* The dominant *REE* cation in this site is Ce, but the Y scattering curve is used, as it most closely resembles the average of all components at this site.

** The multiplicity factor (*M*) is divided by 3 to facilitate comparison with the simplified formula. The ideal *sof* is obtained by dividing the number in this column by 6.

*** The atoms per formula unit (*apfu*) are based on the averaged results of electron-microprobe analyses (EMPA), from column 2 in Table 1 (the crystal used in the crystal-structure refinement).

