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MARIANOITE, A NEW MEMBER OF THE CUSPIDINE GROUP FROM THE PRAIRIE LAKE SILICOCARBONATITE, ONTARIO

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ABSTRACT

Marianoite, a new member of the cuspidine group of minerals, occurs in phlogopite–calcite silicocarbonatite in the western part of the Mesoproterozoic Prairie Lake intrusive complex, in northwestern Ontario, Canada. The mineral forms flattened prismatic crystals with resorbed faces, up to 0.3 mm in length, and is associated with uranoan pyrochlore, titanite and natrolite–muscovite pseudomorphs after xenocrystic nepheline. The crystals are translucent, very pale yellow macroscopically and colorless in plane-polarized light. The mineral is biaxial negative (α 1.700, β 1.715, γ 1.725, $2V_{\text{meas}}$ 80°, $2V_{\text{calc}}$ 78°) and shows a weak optic-axis dispersion ($r < v$). Marianoite is relatively homogeneous in composition; its average empirical formula is $Na_{1.93}(Ca_{4.00}Mn_{0.04})_{\Sigma 4.04}$ $(Nb_{0.97}Zr_{0.90}Ti_{0.09}Fe_{0.08}Mg_{0.03}Hf_{0.01})_{\Sigma 2.08}$ $(Si_{3.97}O_{14})O_{2.93}F_{1.07}$. By analogy with wöhlerite, the simplified formula of marianoite should be written $Na_2Ca_4(Nb,Zr)_2(Si_2O_7)_2(O,F)_4$. The structure of the new mineral species, refined by single-crystal methods to an $R1$ of 4.65% (for $|F_o| > 4\sigma_F$), is monoclinic, space group $P2_1$; the unit-cell parameters are: a 10.8459(15) Å, b 10.2260(14) Å, c 7.2727(10) Å, β 109.332(3)°, V 761.1(3) Å^3 (D_{calc} 3.45 g/cm^3). The mineral is isostructural with wöhlerite [$Na_2Ca_4(Zr,Nb)_2(Si_2O_7)_2(O,F)_4$], but shows the preponderance of Nb in the smallest octahedrally coordinated cation sites in its crystal structure. The occupancy of these sites cannot be determined accurately because of the similar X-ray scattering characteristics and ionic radii of Nb^{5+} and Zr^{4+}. The mineral is named in honor of Anthony Nicola Mariano (b. 1930), in recognition of his contributions to the study of alkaline rocks and carbonatites.

Keywords: marianoite, new mineral species, cuspidine group, crystal structure, silicocarbonatite, Prairie Lake, Ontario, Canada.

SOMMAIRE

On trouve la marianoïte, nouveau membre du groupe de la cuspidine, dans une silicocarbonatite à phlogopite + calcite dans la partie occidentale du complexe intrusif de Prairie Lake, dans le nord-ouest de l'Ontario, au Canada, d'âge mésoprotérozoïque. Le minéral se présente en cristaux prismatiques applattis avec faces résorbées, atteignant jusqu'à 0.3 mm en longueur, et associé au pyrochlore uranifère, titanite, et natrolite + muscovite en pseudomorphose de la népheline, présente en xénocristaux. Les cristaux sont translucides, macroscopiquement jaune très pâle, et incolores en lumière polarisée en plan. Le minéral est biaxe négatif (α 1.700, β 1.715, γ 1.725, $2V_{\text{mes}}$ 80°, $2V_{\text{calc}}$ 78°) et fait preuve d'une faible dispersion des axes optiques $r < v$. La

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marianoïte est relativement homogène en composition; sa formule empirique moyenne serait $Na_{1.93}(Ca_{4.00}Mn_{0.04})_{\Sigma 4.04}$ $(Nb_{0.97}Zr_{0.90}Ti_{0.09}Fe_{0.08}Mg_{0.03}Hf_{0.01})_{\Sigma 2.08}$ $(Si_{3.97}O_{14})O_{2.93}F_{1.07}$. Par analogie avec la wöhlerite, la formule simplifiée de la marianoïte serait $Na_2Ca_4(Nb,Zr)_2(Si_2O_7)_2(O,F)_4$. La structure de la nouvelle espèce, affinée sur monocristal jusqu'à un résidu R1 de 4.65% (pour $|F_o| > 4\sigma_F$), est monoclinique, groupe spatial $P2_1$; les paramètres réticulaires sont: *a* 10.8459(15) Å, *b* 10.2260(14) Å, *c* 7.2727(10) Å, β 109.332(3)°, *V* 761.1(3) Å^3 (D_{calc} 3.45 g/cm^3. Le minéral est isostructural avec la wöhlerite $[Na_2Ca_4(Zr,Nb)_2(Si_2O_7)_2(O,F)_4]$, mais montre une prédominance du Nb aux sites octaédriques les plus petits de sa structure. Le taux d'occupation de ces sites ne peut pas être déterminé avec précision à cause de la dispersion et du rayon ionique semblables de Nb^{5+} et Zr^{4+}. Le nom choisi honore Anthony Nicola Mariano (né en 1930) pour ses contributions à l'étude des roches alcalines et des carbonatites.

Mots-clés: marianoïte, nouvelle espèce minérale, groupe de la cuspidine, structure cristalline, silicocarbonatite, Prairie Lake, Ontario, Canada.

INTRODUCTION

The importance of cuspidine-group minerals as potential repositories for high-field-strength elements (in particular, Nb and Zr) in carbonatites was first recognized by Mariano & Roeder (1989). Although generally not as abundant as pyrochlore or perovskite, Nb- and Zr-rich members of the cuspidine group are a modally significant component of early carbonatites and silicocarbonatites in some localities, which has significant implications for mineral exploration. The cuspidine-group minerals previously reported from carbonatites include cuspidine, niocalite and wöhlerite (Nickel 1956, Mariano & Roeder 1989, Keller *et al.* 1995, Mitchell & Belton 2004). During a detailed mineralogical study of silicocarbonatites from the Prairie Lake complex in northwestern Ontario, we recognized that in addition to wöhlerite, these rocks contain a stoichiometrically similar cuspidine-group mineral consistently showing the predominance of Nb over Zr (in atoms per formula unit, *apfu*). This material was examined in detail and submitted to the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA) as the new species marianoite (марианоит), named for Anthony Nicola ("Tony") Mariano (b. 1930) of Carlisle, Massachusetts, in recognition of his continuing contributions to the mineralogy, geochemistry and economic geology of alkaline rocks and carbonatites. Our proposal (CNMNC no. 2005–05a) was approved in September of 2005. The type material is deposited at the R.B. Ferguson Museum of Mineralogy (University of Manitoba, Winnipeg, Canada) under catalogue no. M 7425.

OCCURRENCE AND PARAGENESIS

The Prairie Lake intrusive complex (Lat. 49°02'N, Long. 86°43'W) is situated immediately northwest of Prairie Lake, some 110 km east of the town of Nipigon in the Thunder Bay district (northwestern Ontario, Canada). The complex comprises predominantly foidolitic and carbonatitic rocks of Mesoproterosoic age, which were emplaced in Archean gneisses of the Superior craton along the Trans-Superior Tectonic Zone (Sage & Watkinson 1991, and references therein). The carbonatitic rocks are most abundant in the peripheral parts of the intrusion, and include modally and texturally diverse sövites, silicocarbonatites and much less abundant dolomite carbonatites. The complex has been a target of intermittent exploration for Nb and U for three decades (Franklin 1978, Mariano 1979, Watkinson 1979). Although pyrochlore is the main mineral of economic interest at Prairie Lake, Mariano & Roeder (1989) have shown that locally, a significant proportion of Nb is bound in wöhlerite, whose modal content reaches 7 vol.% in pseudoleucite-bearing maliginite and some types of silicocarbonatite.

The silicocarbonatite sample containing marianoite was collected by one of us (RHM) from the so-called Tantalum pit south of Anomaly Lake in the western part of the complex. This rock is emplaced in ijolite and consists of euhedral crystals of phlogopite (0.1–5.0 mm across, 55–60 vol.% of the rock), U-rich pyrochlore (20–40 μm across, *ca.* 3 vol.%), titanite (up to 0.6 mm in length, <1 vol.%) and marianoite (up to 0.3 mm in length, *ca.* 1 vol.%) in a mesostasis of inequigranular mosaic-textured calcite (0.2–3.5 mm across, 35–40 vol.%; Fig. 1). Marianoite is an early liquidus mineral in this rock; it crystallized prior to phlogopite, calcite and the bulk of the pyrochlore. Phlogopite is the latest silicate mineral to crystallize. It poikilitically encloses marianoite, pyrochlore, titanite and, locally, calcite. Both phlogopite and calcite host pseudomorphs of natrolite + muscovite after fragmented nepheline, which was undoubtedly derived from the host ijolite. Marianoite forms flattened prismatic crystals with strongly resorbed (?) faces and inclusions of pyrochlore in their peripheral parts (Figs. 1, 2). Parts of the crystals adjacent to pyrochlore are transformed to a turbid fractured material with a low average atomic number (AZ) and H_2O in its chemical composition, as inferred from low analytical totals. The abundance of high-field-strength elements in the pyrochlore and titanite associated with marianoite can be found in Chakhmouradian (2006, Appendix A).

PHYSICAL AND OPTICAL PROPERTIES

Macroscopically, fresh marianoite is very pale yellow and translucent, with a luster ranging from vitreous on

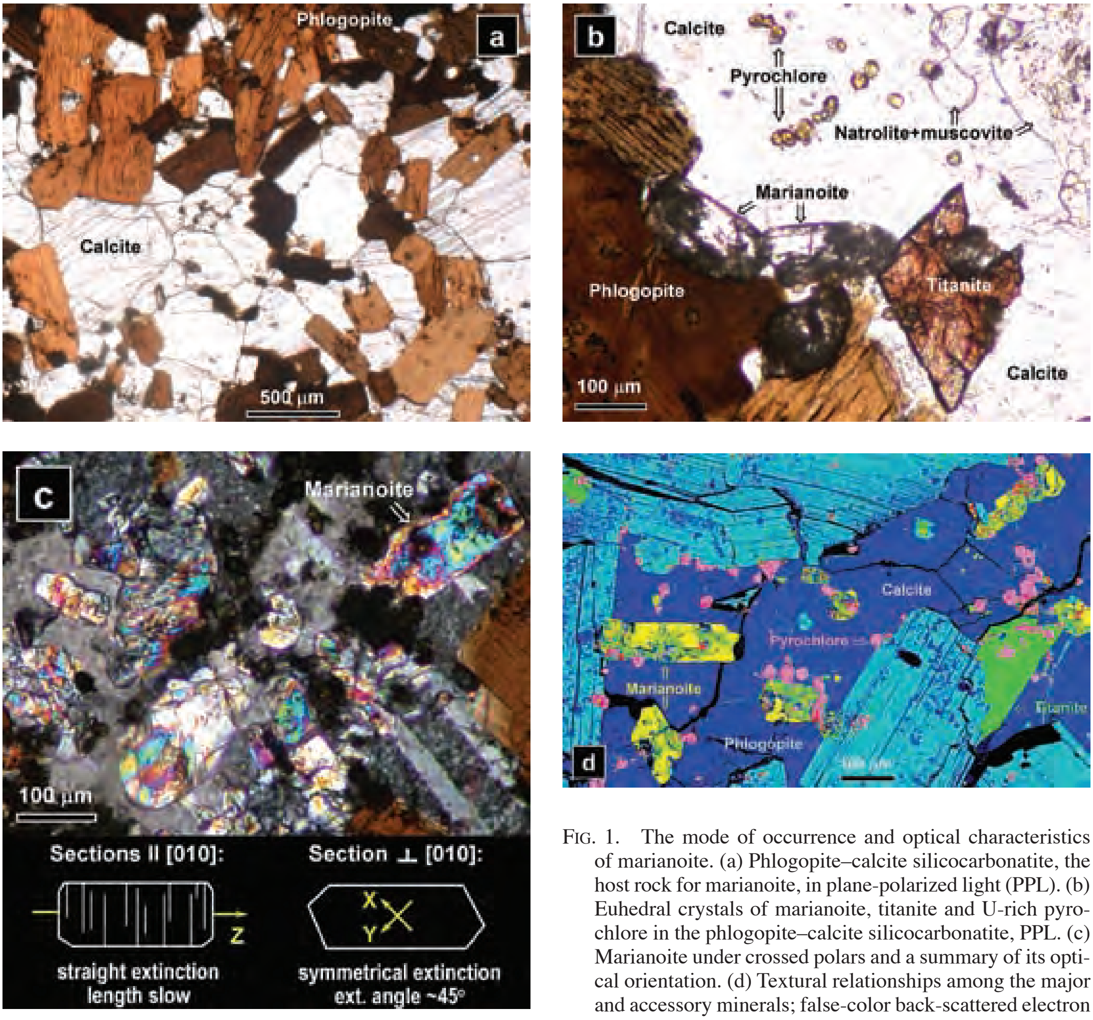

FIG. 1. The mode of occurrence and optical characteristics of marianoite. (a) Phlogopite–calcite silicocarbonatite, the host rock for marianoite, in plane-polarized light (PPL). (b) Euhedral crystals of marianoite, titanite and U-rich pyrochlore in the phlogopite–calcite silicocarbonatite, PPL. (c) Marianoite under crossed polars and a summary of its optical orientation. (d) Textural relationships among the major and accessory minerals; false-color back-scattered electron image. Note radiation damage in marianoite crystals containing inclusions of, or adjacent to, pyrochlore [dark areas in (b) and green fractured areas in (c)].

cleavage surfaces to greasy on resorbed faces. It has a Mohs hardness of 6 (determined with fine-point hardness picks on a polished surface), uneven fracture and a distinct cleavage on {010}. The mineral sinks in di-iodomethane ($D = 3.32$ g/cm^3), but its specific gravity could not be determined more accurately because of the dearth of homogeneous material and lack of suitable heavy liquids; D_{calc} is equal to 3.45(2) g/cm^3. Marianoite is colorless and nonpleochroic in plane-polarized light, and exhibits lamellar twinning in crossed polars. The mineral is biaxial and optically negative, with α 1.700, β 1.715, γ 1.725, $2V_{meas}$ 80°, $2V_{calc}$ 78° and weak optic-axis dispersion ($r < v$). The optic orientation is as follows: $Z = b$, $X \wedge c = 45°$ in acute β (Fig. 1c).

CHEMICAL COMPOSITION

The chemical composition of marianoite was determined by wavelength-dispersive X-ray spectrometry using a fully automated CAMECA SX 100 electron microprobe operated at 15 kV and 20 nA, and a set of well-characterized natural and synthetic standards (Table 1). We used $K\alpha$ analytical lines for F, Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe, and $L\beta$ lines for La, Ce, Nd, Zr, Hf, Nb and Ta. Several grains were analyzed with a 5-µm beam in areas unaffected by alteration,

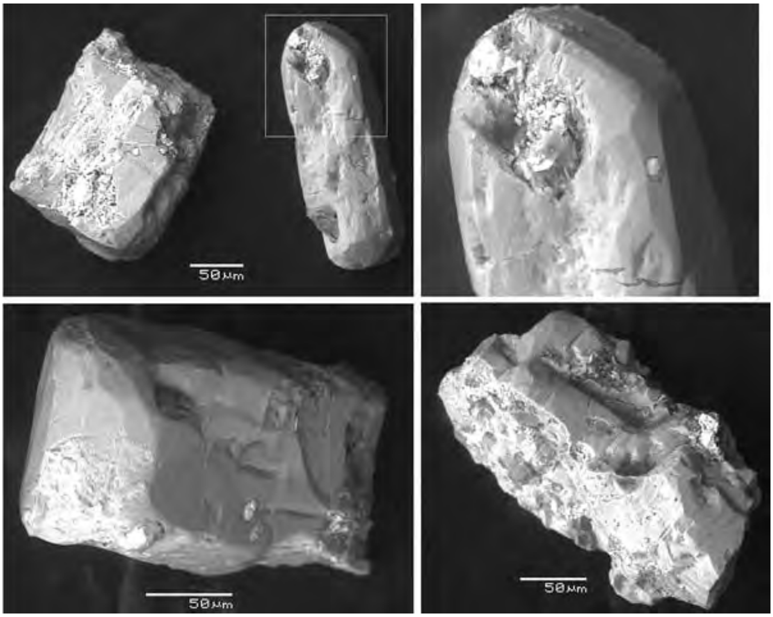

FIG. 2. Morphology of marianoite crystals, as seen in secondary-electron images. Note that some of the crystal faces are smooth and resorbed, whereas other surfaces are fractured and show evidence of radiation damage.

and these data were then used to obtain the average composition listed in Table 1. Detectable zoning was observed in but a few crystals and involves a slight increase in Nb/Zr value from their core rimward. The empirical formula of marianoite, calculated on the basis of 18 anions, is as follows:

TABLE 1. CHEMICAL COMPOSITION OF MARIANOITE

Oxide/ element	Average (16 analyses)	E.s.d.	Range	EMPA standard
Na_2O wt.%	7.45	0.12	7.18 – 7.62	albite
CaO	27.92	0.36	27.49 – 28.86	titanite
MgO	0.14	0.05	0.08 – 0.23	forsterite
MnO	0.37	0.04	0.31 – 0.45	spessartine
FeO	0.72	0.22	0.41 – 1.27	fayalite
TiO_2	0.94	0.35	0.55 – 1.82	titanite
ZrO_2	13.80	0.83	11.42 – 14.77	synthetic ZrO_2
HfO_2	0.15	0.08	0.03 – 0.32	synthetic $HfSiO_4$
Nb_2O_5	16.01	0.49	14.94 – 16.59	syntheticLiNbO$_3$
Ta_2O_5	0.08	0.09	0.00 – 0.26	tantalite-(Mn)
SiO_2	29.68	0.25	29.31 – 30.17	titanite
F	2.54	0.17	2.27 – 2.81	riebeckite
-O=F	21.07			
Total	98.73			

Al, K and light rare-earth elements were sought, but found not to be present above their lower limits of detection (180, 160 and *ca.* 1600 ppm, respectively).

$Na_{1.930}(Ca_{3.996}Mn_{0.042})_{\Sigma 4.038}$ $(Nb_{0.967}Zr_{0.899}Ti_{0.094}Fe_{0.080}Mg_{0.028}Hf_{0.006}Ta_{0.003})_{\Sigma 2.077}$ $(Si_{3.965}O_{14})O_{2.927}F_{1.073}$. Note that the total number of cations in this formula (12.010) is very close to the ideal number (12), as is the *apfu* value for Si, which suggests that all elements present in marianoite in measurable quantities were accounted for in the electron-microprobe analysis. For practical reasons (see below), the simplified formula of marianoite should be written as $Na_2Ca_4(Nb,Zr)_2(Si_2O_7)_2(O,F)_4$. The samples of wöhlerite with a variable Nb:Zr ratio, studied by Mariano & Roeder (1989), show a sympathetic correlation between their Nb and F contents, which suggests the existence of coupled substitution $Zr^{4+} + F^{1-} \rightleftharpoons Nb^{5+} + O^{2-}$ and, thus, some solid solution between $Na_2Ca_4Zr_2(Si_2O_7)_2O_2F_2$ and $Na_2Ca_4Nb_2(Si_2O_7)_2O_4$. This conclusion is further supported by a wide range of Nb/Zr values (0.47–1.33) in these compositionally intermediate minerals (Table 2). Coupled substitutions involving divalent cations may also facilitate the incorporation of Nb in the structure (*e.g.*, $3Zr^{4+} \rightleftharpoons 2Nb^{5+} + Ca^{2+}$) despite appreciable differences in their ionic radii. The remarkable flexibility of cuspidine-type structures allows for the existence of compositions intermediate between cuspidine $[Ca_8(Si_2O_7)_2F_4]$ and niocalite $[Ca_7Nb(Si_2O_7)_2O_3F]$, cuspidine and $NaCa_6Zr(Si_2O_7)_2OF_3$, and niocalite and marianoite (Keller *et al.* 1995, Bellezza *et al.* 2004, Mitchell & Belton 2004; see our Fig. 3). The relative significance of these individual mechanisms of substitution cannot be evaluated at present because of the scarcity of published analytical data for Nb–Zr-rich members of the cuspidine group.

CRYSTALLOGRAPHY

For X-ray-diffraction studies, we selected several clear crystals of marianoite free of inclusions and radiation damage. Because it was impossible to separate any material devoid of {100} twinning, its presence was taken into account in the analysis of the structure. One of the crystals selected was attached to a thin glass rod and mounted on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART charge-coupled-device (CCD) detector, with a crystal-to-detector distance of 5 cm. The application of CCD

TABLE 2. COMPOSITIONS OF CUSPIDINE-GROUP MINERALS WITH VARIOUS Nb:Zr RATIOS: WÖHLERITE, MARIANOITE AND NIOCALITE

	1*	2	3	4‡	5	6	7	8	9	10
Na_2O	7.99	7.55	7.61	7.90	7.21	7.45	7.35	7.25	0.67	0.81
K_2O	0.78	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	tr.	0.35	0.27	0.23	0.12	0.12	0.14	0.19	0.23	0.18
CaO	24.97	25.90	25.26	26.02	26.87	26.32	30.51	28.86	46.39	46.19
MnO	1.66	3.39	1.50	0.90	0.36	0.34	0.38	0.42	0.99	0.49
FeO	0.60	1.54	1.65	1.52	0.89	0.39	0.49	1.27	0.34	0.44
SrO	0.07	n.d.	0.41	n.d.	0.20	0.20	b.d.	b.d.	0.29	0.21
Al_2O_3	1.41	0.05	0.25	n.d.	n.d.	n.d.	n.d.	b.d.	<0.1	n.d.
Y_2O_3	n.d.	n.d.	0.20	0.28	0.06	0.06	b.d.	n.d.	<0.05	<0.05
La_2O_3	n.d.	n.d.	0.11	n.d.	0.03	0.03	b.d.	b.d.	0.24	0.53
Ce_2O_3	1.12	n.d.	0.19	n.d.	0.05	0.05	0.09	b.d.	0.67	1.30
Nd_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	b.d.	b.d.	0.26	0.33
SiO_2	31.92	30.92	30.22	29.75	30.40	30.33	29.54	29.73	29.77	30.01
TiO_2	2.07	2.05	1.96	1.31	0.65	0.51	0.06	1.82	0.15	0.06
ZrO_2	16.35	15.01	13.66	15.26	13.64	14.41	12.97	11.42	0.33	0.23
HfO_2	n.d.	n.d.	0.19	n.d.	0.17	0.17	b.d.	0.32	<0.15	<0.15
Nb_2O_5	8.35	9.21	10.50	12.83	14.50	15.24	16.81	16.32	17.14	16.77
Ta_2O_5	0.73	n.d.	0.27	n.d.	0.21	0.21	0.14	0.03	0.57	0.14
F	1.99	4.18	2.87	2.89	1.92	1.92	1.60	2.81	1.79	1.68
$-O{=}F_2$	0.84	1.76	1.21	1.22	0.81	0.81	0.67	1.18	0.75	0.71
Total	99.90	98.42	95.91	97.67	96.47	96.94	99.41	99.26	99.08	98.66
Na *apfu*	2.016	1.931	2.014	2.064	1.907	1.964	1.911	1.861	0.173	0.210
K	0.130	0.005	-	-	-	-	-	-	-	-
Mg	-	0.069	0.055	0.046	0.024	0.024	0.028	0.038	0.046	0.036
Ca	3.482	3.661	3.693	3.757	3.927	3.834	4.382	4.094	6.612	6.615
Mn	0.183	0.379	0.173	0.103	0.042	0.039	0.043	0.047	0.112	0.055
Fe^{2+}	0.065	0.170	0.188	0.171	0.102	0.044	0.055	0.127	0.038	0.049
Sr	0.005	-	0.032	-	0.016	0.016	-	-	0.022	0.016
Al	0.216	0.008	0.040	-	-	-	-	-	-	-
Y	-	-	0.015	0.020	0.004	0.004	-	-	-	-
La	-	-	0.006	-	0.002	0.002	-	-	0.012	0.026
Ce	0.053	-	0.009	-	0.002	0.002	0.004	-	0.033	0.064
Nd	-	-	-	-	-	-	-	-	0.012	0.016
Si	4.155	4.079	4.124	4.009	4.147	4.123	3.961	3.936	3.960	4.011
Ti	0.203	0.203	0.201	0.133	0.067	0.052	0.006	0.181	0.015	0.006
Zr	1.038	0.966	0.909	1.003	0.907	0.955	0.848	0.737	0.021	0.015
Hf	-	-	0.007	-	0.007	0.007	-	0.012	-	-
Nb	0.491	0.549	0.648	0.782	0.894	0.937	1.019	0.977	1.031	1.013
Ta	0.026	-	0.010	-	0.008	0.008	0.005	0.001	0.021	0.005
Σ	12.063	12.020	12.124	12.088	12.056	12.011	12.262	12.011	12.108	12.137
F	0.819	1.744	1.239	1.226	0.826	0.825	0.678	1.176	0.753	0.710

Columns: wöhlerite (1–6), marianoite (7–8) and niocalite (9–10). 1: from nepheline syenite, Sredne–Tatarskii complex, Siberia, Russia (Sveshnikova & Burova 1973); 2: from nepheline syenite, Mont Saint-Hilaire, Canada (Chao & Gault 1997); 3: from nepheline syenite, Tchivira, Angola (Mariano & Roeder 1989); 4: from nepheline syenite, Brevig, Norway (Mellini & Merlino 1979); 5, 6: from clinopyroxenite, Prairie Lake, Canada (Mariano & Roeder 1989); 7: from calcite carbonatite, Kaiserstuhl, Germany (Keller *et al.* 1995); 8: from phlogopite–calcite silicocarbonatite, Prairie Lake, Canada (composition with the highest Nb:Zr ratio; see Table 1 for the average composition); 9: from calcite carbonatite, Oka complex, Canada (Keller *et al.* 1995); 10: from calcite carbonatite, Kaiserstuhl, Germany (Keller *et al.* 1995). n.d.: no data available, b.d.: below detection limit, tr.: traces. * also contains 0.06 wt.% PbO (0.002 *apfu* Pb) and 0.67 wt.% H_2O^+ (0.582 *apfu* OH); FeO converted from Fe_2O_3 in the original analysis; *apfu* values are approximate because rare-earth elements are reported as ΣREE_2O_3 in the original analysis; ‡ Nb and F values were not determined analytically, but grandfathered from the older literature. The compositions are quoted in wt.% oxides and F; the formulae are recalculated on the basis of 18 anions.

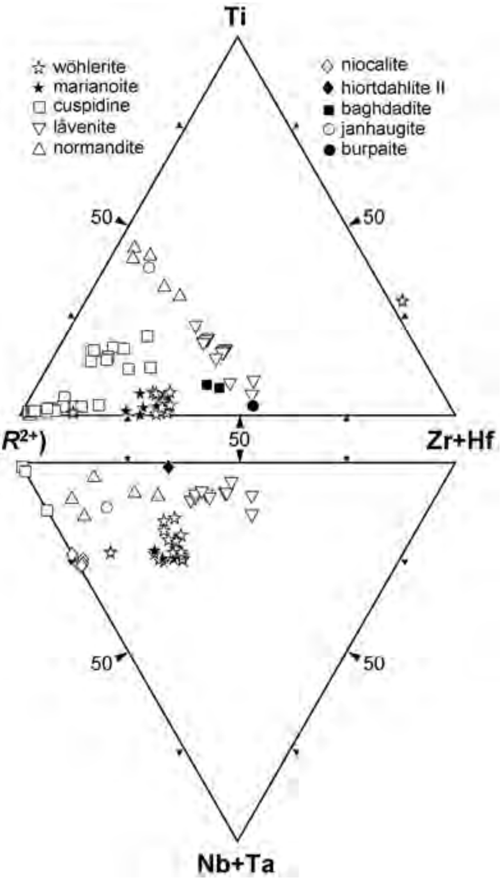

Fig. 3. Compositional variation of cuspidine-group minerals expressed in at.% of the major occupants of octahedrally coordinated cation sites, including Ti, Zr + Hf, Nb + Ta and divalent cations ($^{VI}R^{2+} = {}^{VI}Ca + Mn + Fe + Mg$). The proportion of ^{VI}Ca was calculated as the balance of Ca after the seven- and eight-fold-coordinated sites have been completely filled with Na, K, Sr, Ba and Ca. The data points for marianoite are from this work and that of Keller *et al.* (1995). Other data are from Tikhonenkov & Kazakova (1962), Sveshnikova & Burova (1973), Aarden & Gittins (1974), Polyakov (1974), Mellini & Merlino (1979), Kapustin (1980), Mellini (1981), Annehed *et al.* (1985), Mariano & Roeder (1989), Merlino *et al.* (1990), Keller *et al.* (1995), Moreau *et al.* (1996), Sharygin *et al.* (1996), Chao & Gault (1997), Jamtveit *et al.* (1997), Perchiazzi *et al.* (2000), Bellezza *et al.* (2004) and Mitchell & Belton (2004). The diamond-cored star corresponds to an unnamed mineral compositionally intermediate between wöhlerite and niocalite (Keller *et al.* 1995).

detectors to structure analysis has been discussed in detail by Burns (1998). The X-ray-diffraction data were collected using a monochromatic Mo$K\alpha$ source, frame width of 0.3° in ω, and acquisition time of 30 seconds per frame. A sphere of three-dimensional data was collected, and these data were processed to locate peaks for the determination of unit-cell parameters (Table 3). Three-dimensional data were collected over the interval $3° \leq 2\theta \leq 69.25°$, and then reduced and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. Other experimental details are listed in Table 3.

The structure of marianoite was refined by direct methods in space group $P2_1$ (#4, monoclinic system) using the Bruker SHELXTL Version 5.10 package of programs, incorporating subroutines for the refinement of twinned structures with variable fractional contributions from twin components (Sheldrick 1997). The structure is twinned with twin matrix –1 0 –1, 0 1 0, 0 0 1. Individual twin components refined to 0.357(2) and 0.643(2). The final Flack parameter (Flack 1983) is 0.05(5), indicating that the structure is in the correct absolute orientation. Scattering factors for neutral atoms were taken from Ibers & Hamilton (1974). A table of observed and calculated structure-factors is available from the Depository of Unpublished Data on the MAC website (document Marianoite CM46_1023).

Marianoite is isostructural with wöhlerite (Mellini & Merlino 1979), which corresponds to structure-type #8 in the modular classification of Merlino & Perchiazzi (1988). The atom coordinates and selected bond-lengths for marianoite are given in Tables 4 and 5. This structure can be viewed as consisting of walls of edge-sharing octahedra and sorosilicate groups, both aligned parallel to [001]. The walls are four octahedra wide and interconnected by sharing their corners and through the sorosilicate groups, attached to three adjacent walls simultaneously (Fig. 4). The true coordination of Na atoms is 8, and that of Ca atoms ranges from 6 to 8 (Table 5), but the model presented here is favored by crystallographers for its simplicity and convenience in making structural comparisons among the different members of the cuspidine group (*e.g.*, Merlino & Perchiazzi 1988).

X-ray-diffraction (XRD) data for marianoite were obtained with the Gandolfi method using Ni-filtered Cu$K\alpha$ radiation with a 114.6-mm camera mounted on a Philips 3710 diffractometer operated at 30 mA and 40 kV. The measured *d*-values are in good agreement with those calculated from the single-crystal X-ray-diffraction data (Table 6).

TABLE 3. MARIANOITE: DETAILS OF THE STRUCTURE REFINEMENT

Spacegroup	$P2_1$	Linear absorption	
Unit-cell parameters		Coefficient (μ)	3.33 mm^{-1}
a	10.8459(15) Å	Total reflections	15086
b	10.2260(14) Å	Unique reflections	6188
c	7.2727(10) Å	|Fo| > 4σF	5905
β	109.332(3)°	Final R1 (unique data)	4.94%
V	761.1(3) $Å^3$	Final R1 (|Fo| > 4σF)	4.65%
Z	2	GooF	1.167
Calculated *D*	3.45(2) g/cm^3	Difference peaks	$-1.94e^- Å^{-3}$, $+2.17e^- Å^{-3}$

DISCUSSION

Conditions of crystallization and other localities

The available Sr–Nd isotopic evidence (Bell & Blenkinsop 1987) indicates that the Prairie Lake carbonatites originated from a distinct source in the mantle, in comparison with the coeval alkaline–silicate magmatism in the Midcontinent Rift; Heaman & Machado (1992) provided a detailed discussion of these findings. Chakhmouradian & Mitchell (2002) studied the compositional variation of rock-forming and some accessory minerals from the ijolites and silicocarbonatites (including the marianoite-bearing sample) and concluded that these rocks could not have been derived from the same parental magma and, hence, probably represent two genetically unrelated magma-types. This conclusion is consistent with the published, albeit limited, isotopic data (see above). Chakhmouradian & Mitchell (2002) also showed that the ijolites were disaggregated and intensely digested by the carbonatitic magma, which was the process at least partly responsible for the enrichment of the Prairie Lake carbonatitic magma in silica. The abundance of early-crystallizing titanite in these rocks and the absence of albite in the

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN MARIANOITE

Site	*x*	*y*	*z*	U_{eq}
Na1	0.1306(3)	0.5813(4)	0.4467(6)	0.0135(7)
Na2	0.6243(3)	0.2359(3)	0.6912(5)	0.0145(7)
Ca1	0.3530(2)	0.3468(2)	0.8003(2)	0.0117(3)
Ca2	0.1316(1)	0.5790(2)	0.9463(3)	0.0138(3)
Ca3	0.6551(1)	0.8490(2)	0.7006(2)	0.0129(3)
Ca4	0.1537(2)	0.9684(2)	0.4478(3)	0.0154(3)
*M*1	0.3661(1)	0.7193(1)	0.8045(1)	0.0067(1)
*M*2	0.8413(1)	0.4574(1)	0.0535(1)	0.0093(2)
Si1	0.5721(2)	0.5315(2)	0.6359(3)	0.0083(4)
Si2	0.4204(2)	0.0399(2)	0.8038(3)	0.0088(4)
Si3	0.9345(2)	0.7792(2)	0.1238(3)	0.0084(4)
Si4	0.0597(2)	0.2809(2)	0.4365(3)	0.0105(4)
O1	0.4793(5)	0.4073(4)	0.6178(9)	0.0116(9)
O2	0.0104(5)	0.1383(6)	0.3495(9)	0.0170(12)
O3	0.5183(5)	0.6652(5)	0.6990(9)	0.0188(12)
O4	0.4949(5)	0.1653(5)	0.9178(8)	0.0138(11)
O5	0.4910(5)	0.9025(5)	0.8791(9)	0.0122(9)
O6	0.9724(5)	0.4038(5)	0.3210(8)	0.0164(12)
O7	0.7237(4)	0.5027(6)	0.7729(9)	0.0160(12)
O8	0.2671(5)	0.0427(5)	0.7912(9)	0.0151(11)
O9	0.2062(6)	0.3067(7)	0.4793(11)	0.0227(13)
O10	0.9603(5)	0.6298(6)	0.0741(8)	0.0148(11)
O11	0.0390(5)	0.8813(6)	0.0875(9)	0.0192(12)
O12	0.2540(5)	0.7829(6)	0.9537(8)	0.0157(11)
O13	0.0223(5)	0.2923(5)	0.6374(9)	0.0175(10)
O14	0.5878(6)	0.5622(5)	0.4213(8)	0.0220(11)
O15	0.7928(5)	0.8362(5)	0.0224(10)	0.0154(10)
O16	0.2853(4)	0.5593(5)	0.7754(10)	0.0137(10)
O17	0.2748(5)	0.7841(5)	0.5635(8)	0.0131(10)
F	0.2598(4)	0.5563(4)	0.2536(8)	0.0091(8)

M represents Nb, Zr, Ti, Fe, Mg.

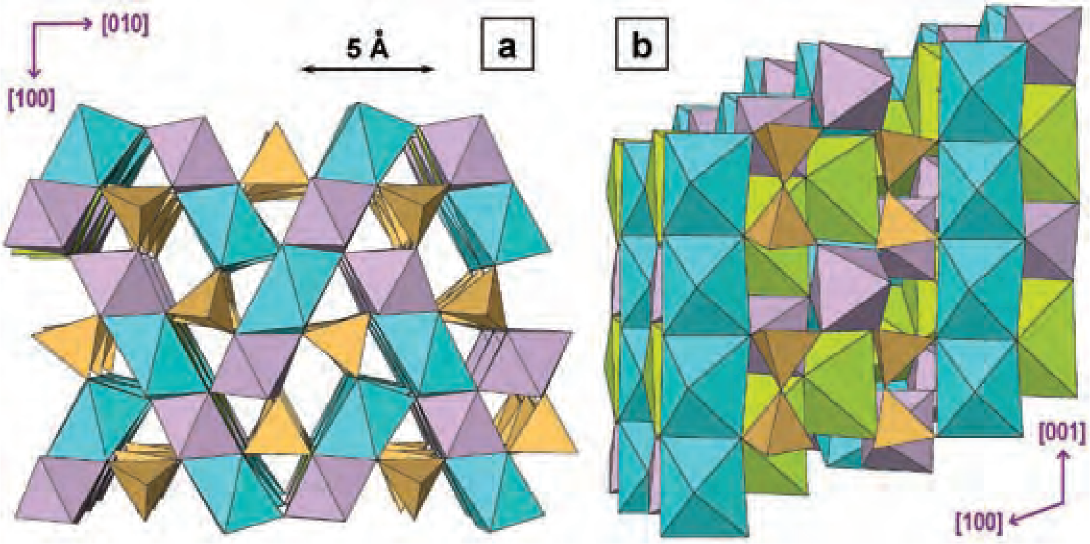

Fig. 4. The crystal structure of marianoite viewed (a) parallel to [001] and (b) at a small angle to [010]. Note the walls consisting of Ca-, Na- and (Nb,Zr)-centered polyhedra (turquoise-blue, olive-green and lavender, respectively) and $(Si_2O_7)^{6-}$ groups (beige) parallel to [001].

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN MARIANOITE

Na1–		Na2–		M1–		M2–	
F	2.303(7)	F	2.186(6)	O17	1.828(5)	O12	2.055(6)
O16	2.434(7)	O1	2.297(6)	O16	1.835(5)	O11	2.055(5)
O6	2.457(7)	O17	2.494(6)	O12	1.988(6)	O6	2.068(5)
O2	2.526(7)	O12	2.527(7)	O3	2.111(6)	O7	2.070(6)
O17	2.567(6)	O4	2.596(6)	O4	2.154(5)	O8	2.074(6)
O13	2.666(6)	O14	2.805(7)	O5	2.269(5)	O10	2.160(6)
O10	2.772(7)	O3	2.839(8)				
O9	2.913(8)	O7	2.922(7)				
ave.	2.580	ave.	2.583	ave.	2.031	ave.	2.080
Ca1–		Ca2–		Ca3–		Ca4–	
O16	2.282(5)	F	2.219(6)	F	2.292(5)	O2	2.282(6)
O1	2.285(6)	O2	2.275(6)	O15	2.326(6)	O17	2.292(6)
O15	2.351(7)	O10	2.393(6)	O9	2.338(7)	O7	2.425(6)
O4	2.383(6)	O16	2.395(6)	O1	2.368(6)	O8	2.508(6)
O9	2.386(7)	O12	2.463(6)	O3	2.392(6)	O13	2.548(6)
O5	2.452(6)	O15	2.602(6)	O5	2.585(6)	O6	2.580(6)
		O11	2.697(6)			O11	2.655(6)
						O14	2.814(6)
ave.	2.356	ave.	2.435	ave.	2.384	ave.	2.513
Si1–		Si2–		Si3–		Si4–	
O1	1.598(5)	O4	1.593(5)	O15	1.579(5)	O9	1.536(6)
O3	1.612(6)	O5	1.608(5)	O10	1.616(6)	O2	1.610(6)
O7	1.643(5)	O14	1.626(6)	O11	1.626(6)	O6	1.629(6)
O14	1.655(6)	O8	1.635(6)	O13	1.648(6)	O13	1.645(7)
ave.	1.627	ave.	1.616	ave.	1.617	ave.	1.605

TABLE 6. X-RAY-DIFFRACTION (GANDOLFI) PATTERN OF MARIANOITE

I	d_{meas}	d_{calc}	*hkl*	I	d_{meas}	d_{calc}	*hkl*
m	3.64	3.62	220	m	2.10	2.10	302
m	3.23	3.23	130	**s**	**2.02**	**2.01**	**232, $\bar{4}$32**
s	**3.04**	**3.05**	**$\bar{1}$31, 031**	w	1.945	1.940	322
s	**2.98**	**2.97**	**102**	m	1.820	1.820	$\bar{2}$04
		2.96	**$\bar{3}$02**	w	1.782	1.781	$\bar{5}$32
s	**2.85**	**2.84**	**320, 230**	w	1.758	1.757	052
m	**2.48**	**2.49**	**$\bar{1}$32**	w	1.690	1.687	422
		2.48	**410**	m	1.539	1.534	124
m	2.42	2.42	032, $\bar{2}$32	m	1.525	1.526	062, $\bar{2}$62
w	2.30	2.29	240			1.525	360

Peak intensity (estimated visually from film): s: strong, m: medium, w: weak. The strongest five lines are indicated in bold. Values of *d* are quoted in Å.

nepheline-replacement assemblage (see OCCURRENCE AND PARAGENESIS) indicate log $a(SiO_2)$ values in the range from –1.2 to –0.7 at T = 900–1000 K (Barker 2001). That the Nb–Zr silicate marianoite precipitated earlier than pyrochlore also indicates initially high $a(SiO_2)$ in the magma.

Although not as well studied as *bona fide* carbonatites, silicocarbonatites are relatively common and may have a multiplicity of origins (*e.g.*, direct crystallization of carbonate–silicate melts, fractionation of silicate minerals from carbonatitic magma, or contamination of carbonatitic magma by wallrock silicate material). Thus, carbonatitic magmas of different provenance can potentially attain the level of silica activity necessary to stabilize Nb–Zr silicates and titanite on the liquidus. Crystal fractionation appears to be responsible for the formation of niocalite-bearing parageneses in natrocarbonatites at Oldoinyo Lengai in Tanzania (Mitchell & Belton 2004), whereas wallrock assimilation probably enhanced the activity of silica in silicocarbonatites at Prairie Lake and Kaiserstuhl, Germany (Keller *et al.* 1995). In addition to niocalite, the latter locality contains phases intermediate in composition with respect to niocalite and wöhlerite (Keller *et al.* 1995). Although neither optical nor XRD data are available for the wöhlerite-like mineral from Kaiserstuhl, it consistently shows Nb > Zr in the formula and, hence, should be reclassified as marianoite (Table 2, no. 7). Marianoite has also been tentatively identified in calcite carbonatite from Okorusu in Namibia (A.N. Mariano, pers. commun.).

Nomenclature

Mellini & Merlino (1979) refined the crystal structure of wöhlerite from its type locality at Langesundfjord, Norway, and proposed that Nb + Ti and Zr in this mineral are completely ordered over the two smallest octahedrally coordinated sites (designated as *M*1 and *M*2 in Tables 4 and 5). The proportion of Nb and Zr at these sites cannot be refined directly because of the very similar X-ray-scattering characteristics of the two elements. Accordingly, the interpretation of Mellini & Merlino stems from the following evidence:

(1) The $M1O_6$ polyhedron is smaller in comparison with the $M2O_6$ polyhedron;

(2) The *M*1–O distances (1.84–2.26 Å) are more variable than the *M*2–O distances (2.05–2.16 Å);

(3) The *M*1 site is characterized by a significantly larger equivalent thermal parameter (0.74 Å^2 *versus* 0.42 Å^2 for *M*2).

The formula of wöhlerite had, until very recently, been given as $NaCa_2(Zr,Nb)(Si_2O_7)(O,F)_2$ or any even multiples thereof (Anthony *et al.* 1995, Gaines *et al.* 1997, Mandarino 1999, PDF #10–0462, among others). It is only in the 2004 edition of *Fleischer's Glossary of Mineral Species* (Mandarino & Back 2004) that the formula of wöhlerite was unilaterally revised to include independent Zr and Nb sites, *i.e.*, $Na_2Ca_4Zr(Nb,Ti)(Si_2O_7)_2(O,F)_4$. Because the aforementioned arguments of Mellini & Merlino (1979) are pivotal to the discussion of the structural role of Nb and Zr in wöhlerite and, hence, the validity of marianoite as a mineral species, we shall address these arguments in detail below.

(1) *Size difference*. The average *M*1–O distance in both wöhlerite and marianoite is about 0.05 Å shorter than the average *M*2–O distance. However, the statement of Mellini & Merlino (1979, p. 118) that the average *M*–O distances are "in close agreement with the values calculated for the proposed site occupancies on the basis of the effective ionic radii" is not accurate. If the occupancy of the *M*1 site in wöhlerite is $(Nb_{0.8}Ti_{0.2})$ (Mellini & Merlino 1979, p. 119), the average *M*1–O distance should be 1.99 Å (ionic radii from Shannon 1976). If the proportion of Ti at this site is fixed at 20%, the average *M*1–O distance of 2.033 Å requires that the remainder be made up of 50% Zr and 30% Nb. Clearly, this result is at variance with the interpretation of Mellini & Merlino (1979) that the *M*1 site is populated predominantly by Nb. It is also pertinent to the present discussion that these authors did not analyze their wöhlerite sample for Nb, assuming that its Nb content was the average of the values obtained by Brögger & Cleve (1890) and Tschernik (1909) on different material by "wet" chemical methods. A scrutiny of the literature shows that in cuspidine-group minerals, the size of $(Nb,Zr,Ti)O_6$ polyhedra is not a reliable measure of site occupancy. For example, the average Nb–O distance in niocalite is 0.05 Å longer than the calculated value, whereas the average Zr–O distance in hiortdahlite II is 0.07 Å longer than expected (Mellini 1982, Merlino & Perchiazzi 1987).

(2) *Bond-length variations*. Displacement of a cation from the center of its coordination polyhedron, resulting in deviations of bond lengths from the average value, is controlled by a number of parameters, both intrinsic (*e.g.*, mismatch between the size of the actual occupant and the optimal size of the cation for this particular site) and extrinsic (*e.g.*, electrostatic forces exerted by ions outside the nearest coordination-sphere). It is unreasonable to expect that Nb^{5+} is *invariably* displaced from the center of its coordination polyhedron more than Zr^{4+}. For example, the shortest and longest Zr–O bonds in ZrO_6 polyhedra in the structure of $PbZrO_3$ differ by 0.14 Å (2.03 *versus* 2.17 Å: Teslic & Egami 1998). The same magnitude of variation is observed for Nb–O bonds in the structure of $NaNbO_3$ (1.94 *versus* 2.08 Å: Xu *et al.* 2003), which was used by Mellini & Merlino (1979) to support their argument for complete Nb–Zr order in wöhlerite. There are many examples among niobosilicate minerals in which the difference between the longest and shortest Nb–O distances is within the value observed for the *M*2 site in the present work (*e.g.*, Piilonen *et al.* 2000). Thus, bond-length variations cannot reliably be used to constrain the proportion of Zr and Nb at the *M* sites.

(3) *Difference in thermal parameters*. The equivalent thermal parameters at the *M*1 and *M*2 sites obtained in the present work show a relation opposite to that observed by Mellini & Merlino (1979), *i.e.*, our $U_{eq}(M1)$ value is 1.4 times *smaller* than $U_{eq}(M2)$ (Table 4). If we accept the explanation of Mellini & Merlino (1979, p. 119) explanation that increasing U_{eq} correlates with the "offsetting" effect of Nb^{5+}, the higher $U_{eq}(M2)$ value in our refinement would imply the presence of significant Nb at that site. That thermal parameters show no consistent behavior in the two types of material structurally studied suggests that they should not be used to support any cation-assignment model.

From the above discussion, it is clear that partitioning of Nb and Zr between the two smallest octahedrally coordinated sites in the wöhlerite–marianoite series cannot be determined unambiguously, even in cases where high-quality structural data are available. The CNMNC IMA recommends that such minerals be treated as containing a "composite site" made up of two or more crystallographic sites with indeterminate cation-occupancies (Nickel & Grice 1998, p. 917).

This nomenclatural approach is used for amphiboles, micas, staurolite and many other minerals in which the assignment of cations to discrete crystallographic sites is problematic or would cause unwarranted proliferation of mineral species. Applying the same approach to the wöhlerite–marianoite series seems both rational (see above) and practical. First of all, having one "composite site" restricts the number of end members to two or, possibly, three [Zr > (Nb,Ti), Nb > (Zr,Ti) and Ti > (Zr,Nb)]. Recognition of the two small octahedral sites as distinct constituents of the formula can potentially spawn a multitude of mineral species: nine featuring various combinations of Zr, Nb and Ti in *M*1 and *M*2, and many more if any element other than Zr, Nb or Ti is found to occupy >50% of *either* one of these sites. The use of chemical data as the primary basis for classification is more practical also because it does not require a laborious and costly structural investigation of the material in question. Lastly, our simplified scheme of classification is in keeping with, and will not require a revision of, the conventionally accepted formula of wöhlerite [$NaCa_2(Zr,Nb)(Si_2O_7)(O,F)_2$].

In conclusion, we wish to add that the literature concerning the crystal chemistry of cuspidine-group minerals lacks convincing empirical evidence that differences in cation radius can drive the ordering of Zr, Nb and Ti over the small octahedrally coordinated sites. For example, the Zr-dominant låvenite and Ti-dominant normandite form a continuous solid-solution, observable, in some cases, within a single zoned crystal (Moreau *et al.* 1996, Perchiazzi *et al.* 2000). Given a difference of 16% between the ionic radii of $^{[6]}Zr^{4+}$ and $^{[6]}Ti^{4+}$, it is difficult to explain why these minerals, which crystallized under the same geological conditions as wöhlerite, lack detectable order in their distribution of cations. Extensive substitutions of Zr and Nb for Ca in cuspidine, Zr for Ca in niocalite, and Zr + Nb for Ti in janhaugite (Annehed *et al.* 1985, Keller *et al.* 1995, Sharygin *et al.* 1996, Bellezza *et al.* 2004, Mitchell & Belton 2004) attest to the great structural flexibility of these minerals and the complexity of substitution mechanisms involving Zr, Nb and Ti (Fig. 3). The limited analytical data presently available for the wöhlerite–marianoite series span the range $0.5 \leq Nb/Zr \leq 1.3$ (Table 2), and it is clearly a matter of time before more Zr-rich and Nb-rich members are found.

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REFERENCES

AARDEN, H.M. & GITTINS, J. (1974): Hiortdahlite from Kipawa River, Villedieu Township, Temiskaming County, Québec, Canada. *Can. Mineral.* **12**, 241-247.

ANNEHED, H., FÄLTH, L. & RAADE, G. (1985): The crystal structure of janhaugite, a sorosilicate of the cuspidine family. *Neues Jahrb. Mineral., Monatsh.*, 7-18.

ANTHONY, J.W., BIDEAUX, R.A., BLADH, K.W. & NICHOLS, M.C. (1995): *Handbook of Mineralogy.* **II**. *Silica, Silicates.* Mineral Data Publ., Tucson, Arizona.

BARKER, D.S. (2001): Calculated silica activities in carbonatite liquids. *Contrib. Mineral. Petrol.* **141**, 704-709.

BELL, K. & BLENKINSOP, J. (1987): Archean depleted mantle: evidence from Nd and Sr initial isotopic ratios of carbonatites. *Geochim. Cosmochim. Acta* **51**, 291-298.

BELLEZZA, M., MERLINO, S. & PERCHIAZZI, N. (2004): Chemical and structural study of the Zr,Ti-disilicates in the venanzite from Pian di Celle, Umbria, Italy. *Eur. J. Mineral.* **16**, 957-969.

BRÖGGER, W.C. & CLEVE, P.T. (1890): Die Mineralien der Syenitpegmatitgänge der Südnorwegischen Augit- und Nephelinsyenite. *Z. Krystallogr. Mineral.* **16**, 1-658.

BURNS, P.C. (1998): CCD area detectors of X-rays applied to the analysis of mineral structures. *Can. Mineral.* **36**, 847-853.

CHAKHMOURADIAN, A.R. (2006): High-field-strength elements in carbonatitic rocks: geochemistry, crystal chemistry and significance for constraining the sources of carbonatites. *Chem. Geol.* **235**, 138-160.

CHAKHMOURADIAN, A.R. & MITCHELL, R.H. (2002): The mineralogy of carbonatites and related rocks from the Prairie Lake complex, northwestern Ontario. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **27**, 46.

CHAO, G.Y. & GAULT, R.A. (1997): Normandite, the Ti-analogue of låvenite from Mont Saint-Hilaire, Quebec. *Can. Mineral.* **35**, 1035-1039.

FLACK, H.D. (1983): On enantiomorph-polarity estimation. *Acta Crystallogr.* **A39**, 876-881.

FRANKLIN, J.M. (1978): Uranium mineralization in the Nipigon area, Thunder Bay District, Ontario. *Geol. Surv. Can., Pap.* **78-1A**, 275-282.

GAINES, R.V., SKINNER, H.C.W., FOORD, E.E., MASON, B. & ROSENZWEIG, A. (1997): *Dana's New Mineralogy.* John Wiley & Sons, Inc., New York, N.Y.

HEAMAN, L.M. & MACHADO, N. (1992): Timing and origin of midcontinent rift alkaline magmatism, North America: evidence from the Coldwell Complex. *Contrib. Mineral. Petrol.* **110**, 289-303.

IBERS, J.A. & HAMILTON, W.C. (1974): *International Tables for X-ray Crystallography* **IV**. Kynoch Press, Birmingham, U.K.

JAMTVEIT, B., DAHLGREN, S. & AUSTRHEIM, H. (1997): High-grade contact metamorphism of calcareous rocks from the Oslo Rift, southern Norway. *Am. Mineral.* **82**, 1241-1254.

KAPUSTIN, YU.L. (1980): Götzenite and wöhlerite from the alkaline massifs of Sangilen (Tuva). *Zap. Vses. Mineral. Obshchest.* **109**, 594-599.

KELLER, J., WILLIAMS, C.T. & KOBERSKI, U. (1995): Niocalite and wöhlerite from the alkaline and carbonatite rocks at Kaiserstuhl, Germany. *Mineral. Mag.* **59**, 561-566.

MANDARINO, J.A. (1999): *Fleischer's Glossary of Mineral Species*. The Mineralogical Record Inc., Tucson, Arizona.

MANDARINO, J.A. & BACK, M.E. (2004): *Fleischer's Glossary of Mineral Species*. The Mineralogical Record Inc., Tucson, Arizona.

MARIANO, A.N. (1979): Petrographic examination of selected rocks and drill core from the Prairie Lake Carbonatite Complex, Ontario, Canada. *Unpubl. Rep. to Union Oil of Canada, Ltd.*

MARIANO, A.N. & ROEDER, P.L. (1989): Wöhlerite: chemical composition, cathodoluminescence and environment of crystallization. *Can. Mineral.* **27**, 709-720.

MELLINI, M. (1981): Refinement of the crystal structure of låvenite. *Tschermaks Mineral. Petrogr. Mitt.* **28**, 99-112.

MELLINI, M. (1982): Niocalite revisited: twinning and crystal structure. *Tschermaks Mineral. Petrogr. Mitt.* **30**, 249-266.

MELLINI, M. & MERLINO, S. (1979): Refinement of the crystal structure of wöhlerite. *Tschermaks Mineral. Petrogr. Mitt.* **26**, 109-123.

MERLINO, S. & PERCHIAZZI, N. (1987): The crystal structure of hiortdahlite II. *Mineral. Petrol.* **37**, 25-35.

MERLINO, S. & PERCHIAZZI, N. (1988): Modular mineralogy in the cuspidine group of minerals. *Can. Mineral.* **26**, 933-943.

MERLINO, S., PERCHIAZZI, N., KHOMYAKOV, A.P., PUSHCHAROVSKII, D.Y., KULIKOVA, I.M. & KUZMIN, V.I. (1990): Burpalite, a new mineral from Burpalinskii massif, North Transbajkal, USSR: its crystal structure and OD character. *Eur. J. Mineral.* **2**, 177-185.

MITCHELL, R.H. & BELTON, F. (2004): Niocalite–cuspidine solid solution and manganoan monticellite from natrocarbonatite, Oldoinyo Lengai, Tanzania. *Mineral. Mag.* **68**, 787-799.

MOREAU, C., OHNENSTETTER, D., DEMAIFFE, D. & ROBINEAU, B. (1996): The Los Archipelago nepheline syenite ring-structure: a magmatic marker of the evolution of the central and equatorial Atlantic. *Can. Mineral.* **34**, 281-299.

NICKEL, E.H. (1956): Niocalite – a new calcium niobium silicate mineral. *Am. Mineral.* **41**, 785-786.

NICKEL, E.H. & GRICE, J.D. (1998): The IMA Commission on New Minerals and Mineral Names – procedures and guidelines on mineral nomenclature, 1998. *Can. Mineral.* **36**, 913-926.

PERCHIAZZI, N., MCDONALD, A.M., GAULT, R.A., JOHNSEN, O. & MERLINO, S. (2000): The crystal structure of normandite and its crystal-chemical relationships with låvenite. *Can. Mineral.* **38**, 641-648.

PIILONEN, P.C., LALONDE, A.E., MCDONALD, A.M. & GAULT, R.A. (2000): Niobokupletskite, a new astrophyllite-group mineral from Mont Saint-Hilaire, Quebec, Canada: description and crystal structure. *Can. Mineral.* **38**, 627-639.

POLYAKOV, K.I. (1974): Wöhlerite from alkaline rocks of the Turiy Mys (Kola Peninsula). *In* Alkaline Rocks of the Kola Peninsula. Nauka Press, Leningrad, USSR (112-117; in Russ.).

SAGE, R.P. & WATKINSON, D.H. (1991): Alkalic rock – carbonatite complexes of the Superior Structural Province northern Ontario, Canada. *Chron. Rech. Min.* **504**, 5-19.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

SHARYGIN, V.V., STOPPA, F. & KOLESOV, B.A. (1996): Zr–Ti disilicates from the Pian di Celle volcano, Umbria, Italy. *Eur. J. Mineral.* **8**, 1199-1212.

SHELDRICK, G.M. (1997): SHELXTL *Reference Manual*. Bruker-AXS, Inc., Madison, Wisconsin.

SVESHNIKOVA, E.V. & BUROVA, T.A. (1973): Minerals of the wöhlerite group and titan-rosenbuschite from nepheline syenites of Trans-Angara. *Trudy Mineral. Muzeya Russ. Acad. Sci.* **22**, 119-123 (in Russ.).

TESLIC, S. & EGAMI, T. (1998): Atomic structure of $PbZrO_3$ determined by pulsed neutron diffraction. *Acta Crystallogr.* **B54**, 750-765.

TIKHONENKOV, I.P. & KAZAKOVA, M.E. (1962): Wöhlerite from alkaline pegmatites of the Eastern Sayan. *Trudy Inst. Mineral. Geokhim. Kristallokhim. Red. Elem.* **9**, 83-87 (in Russ.).

TSCHERNIK, G. (1909): Mosandrite and wöhlerite. *Bull. Acad. Imp. Sci. St. Petersburg* **3**, 903-925.

WATKINSON, D.H. (1979): Uranium mineralization in the Prairie Lake alkalic rock – carbonatite complex, northwestern Ontario. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.*, 85.

XU, HONGWU, SU, YALI, BALMER, M.L. & NAVROTSKY, A. (2003): A new series of oxygen-deficient perovskites in the $NaTi_xNb_{1-x}O_{3-0.5x}$ system: synthesis, crystal chemistry, and energetics. *Chem. Mater.* **15**, 1872-1878.

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