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

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INTRODUCTION

In their paper entitled "Marianoite, a new member of the cuspidine group from the Prairie Lake silicocarbonatite, Ontario", Chakhmouradian *et al.* (2008) presented chemical, crystallographic and structural data on what they claimed is a new mineral species in the cuspidine group. All the phases in this group are built up of "octahedral" walls four columns wide, and disilicate groups. Merlino & Perchiazzi (1988) derived ten distinct structural types, which result from the different ways to connect disilicate groups and "octahedral" walls, and present different unit-cell parameters and space-group symmetries. "Marianoite", with chemical composition $Na_{1.930}Ca_{3.996}Mn_{0.042}Nb_{0.967}Zr_{0.889}Ti_{0.094}Fe_{0.080}Mg_{0.028}Hf_{0.006}Ta_{0.003}(Si_{3.965}O_{14})(O_{2.927}F_{1.073})$, belongs to structural type 8 in that modular classification, together with wöhlerite. The chemical, crystallographic (Table 1) and structural data point to very close relationships between them, more precisely an actual identity, in our view, with no need for the introduction of a new, redundant species. The structural study of wöhlerite was carried out on a crystal from Brevig, Norway (Mellini & Merlino 1979), with data collected with a Philips PW 1100 automatic diffractometer [graphite monochromatized Mo*K*α radiation; θ–2θ scan, scan width 2.00°, scan speed 0.08° s^{-1}, from 2 to 30° in θ; absorption correction by the method of North *et al.* (1968)]. The structural study on "marianoite" was carried on crystal from Prairie Lake with data collected on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD detector [monochromatized Mo*K*α radiation; frame width of 0.3° in ω; acquisition time of 30 seconds per frame; data collected in the interval 3 to 69.25° in 2θ). During the refinement, account was taken of {100} twinning (fractional contributions of the twin components: 0.357 and 0.643)]. The cation distributions in the "octahedral" walls is represented in Figure 1. The atomic positions are denoted in different ways in the papers by Chakhmouradian *et al.* (2008) and Mellini & Merlino (1979). In Table 2, we compare the notations given in the two papers for corresponding atomic positions.

The only substantial differences are not in the data obtained through the X-ray-diffraction study but only in the crystal-chemical interpretation of the results by Mellini & Merlino (1979) on one hand and Chakhmouradian *et al.* (2008) on the other; the different interpretations may be easily appreciated by looking at the ideal crystal-chemical formulas presented by the two groups of authors, with attention to the cations in brackets:

wöhlerite (Mellini & Merlino 1979)
$Na_2Ca_4[Zr(Nb_{0.8}Ti_{0.2})](Si_2O_7)_2(O_{2.8}F_{1.2})$

"marianoite" (Chakhmouradian *et al.* 2008)
$Na_2Ca_4[Nb,Zr]_2 \qquad (Si_2O_7)_2(O,F)_4$

TABLE 1. CELL PARAMETERS AND RESULTS OF THE STRUCTURE REFINEMENTS FOR WÖHLERITE AND "MARIANOITE"

	wöhlerite	"marianoite"
space group	*P*2_1	*P*2_1
a (Å)	10.823(3)	10.8459(19)
b (Å)	10.244(3)	10.2260(14)
c (Å)	7.290(2)	7.2727(10)
β (°)	109.00(4)	109.332(3)
Unique reflections	2343	5905
Final R_1 [Fo > 4σ(Fo)]	0.019	0.0465
Residual peaks (e·Å^{-3})	no peak larger than 0.03	+2.17, –1.94

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In particular, according to Mellini & Merlino (1979), zirconium and niobium (plus minor titanium) are well ordered at distinct sites, whereas according to Chakhmouradian *et al.* (2008), zirconium and niobium are randomly distributed on the two sites. Notwithstanding the similar, nearly identical, scattering power of zirconium and niobium, Mellini & Merlino (1979) maintained that the ordered distribution of Zr and Nb + Ti atoms between the two smallest sites in the "octahedral" walls may be reliably established on the basis of a) average bond-distances involving the two sites, b) different site-distortion, c) different thermal parameters for the atoms at the two sites. The arguments of Mellini & Merlino (1979) were rejected by Chakhmouradian *et al.* (2008), who maintained that the partitioning of Nb and Zr between the two smallest octahedrally coordinated sites cannot be determined unambiguously and that the mineral has to be treated as containing a "composite site" made up of the two crystallographic sites we are discussing, with Zr, Nb (and Ti) randomly distributed between them. Following this approach, wöhlerite would contain zirconium dominant at both sites, whereas "marianoite" would contain niobium dominant at both sites, and consequently deserve the status of a new mineral species.

DISCUSSION

In the following, we shall confirm our interpretation, presenting more detailed evidence for it and pointing out the flaws in the critical remarks by Chakhmouradian *et al.* (2008). As the substantial differences between our interpretation and that by Chakhmouradian *et al.* (2008) lies in the different partitioning of Nb^{5+} and Zr^{4+} cations, we shall first of all present the bond distances, their average values, as well as the site distortion (measured by δ, the difference between the largest and shortest bond-distances) at the *M*1 and *M*2 sites, together with the corresponding values in two typical zirconium and niobium minerals of the cuspidine group, låvenite (Mellini 1981) and niocalite (Mellini 1982), respectively.

On the basis of the data presented in Table 3, we proceed to compare the agreement of the experimental results with the suggested partitioning.

Bond distances

The "effective ionic radii" of Nb^{5+}, Ti^{4+} and Zr^{4+} in coordination VI (Shannon & Prewitt 1969, Shannon 1976) are: 0.64, 0.605, 0.72 Å, and the ionic radius of ${}^{IV}O^{2-}$ is 1.378 Å (Shannon & Prewitt 1969) [Chakhmouradian *et al.* (2008) have carried on their calculation erroneously assuming an "effective ionic radius" for the O^{2-} anion of 1.365 Å, corresponding to the ionic radius of ${}^{III}O^{2-}$; actually, the oxygen anions are in fourfold coordination, the only exception being O8 (O5 in wöhlerite)].

Assuming the cationic distribution proposed by Mellini & Merlino (1979) [Zr at *M*2 and ($Nb_{0.8}Ti_{0.2}$) at *M*1] and applying their indication also in the case of "marianoite" [Zr at *M*2 and Nb at *M*1], the calculated average bond-distances (in Å) are:

	wöhlerite		"marianoite"	
	calc.	obs.	calc.	obs.
*M*1–O	2.011	2.033	2.018	2.031
*M*2–O	2.098	2.084	2.098	2.080

The discrepancies between calculated and observed values are –0.022 and 0.014 for *M*1 and *M*2, respectively, in wöhlerite ($\Sigma\Delta^2 = 0.68 \times 10^{-3}$) and –0.013 and 0.018 for *M*1 and *M*2, respectively, in "marianoite" ($\Sigma\Delta^2 = 0.49 \times 10^{-3}$).

By assuming a disordered distribution of the cations between the two sites, we obtain:

	wöhlerite		"marianoite"	
	calc.	obs.	calc.	obs.
*M*1–O	2.055	2.033	2.058	2.031
*M*2–O	2.055	2.084	2.058	2.080

The discrepancies between calculated and observed values are 0.022 and –0.029 for *M*1 and *M*2, respectively, in wöhlerite ($\Sigma\Delta^2 = 1.33 \times 10^{-3}$); 0.027 and –0.022 Å for *M*1 and *M*2, respectively, in "marianoite" ($\Sigma\Delta^2 = 1.21 \times 10^{-3}$).

Thus the crystal-chemical interpretation by Mellini & Merlino (1979) is still to be preferred with respect to that by Chakhmouradian *et al.* (2008). The critical remarks by those authors cannot alter this conclusion. Moreover, we may use their arguments about the occupancy of site *M*1 in wöhlerite, obviously assuming the

TABLE 2. NOTATIONS FOR CORRESPONDING ATOMIC POSITIONS IN "MARIANOITE" AND WÖHLERITE

"Marianoite"	Ca1	Ca2	Ca3	Ca4	Na1	Na2	Si1	Si2	Si3	Si4	*M*1	*M*2
Wöhlerite	Ca2	Ca3	Ca4	Ca1	Na2	Na1	Si2	Si1	Si4	Si3	Nb	Zr

"Marianoite"	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	O14	O15	O16	O17	F
Wöhlerite	O2	O7	O4	O3	O1	O9	O6	O5	O11	O8	O10	O13	O18	O17	O12	O16	O14	F15

correct radius for the O^{2-} anion, to definitively validate our cation distribution. In fact, they maintain that "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" (Chakhmouradian *et al.* 2008). Actually, if the proportion of Ti at the *M*1 site is fixed at 20%, the average *M*1–O distance of 2.033 Å requires that the remainder be made up of 53% Nb and 27% Zr.

The conclusion by Chakhmouradian *et al.* (2008) that "clearly, this result is at variance with the interpretation of Mellini & Merlino (1979) that the *M*1 site is populated predominantly by Nb" may be fully reversed; merely on the basis of their argument, we may conclude that the *M*1 site in wöhlerite is predominantly populated by Nb.

Site distortion

The *M*1 and *M*2 sites are substantially different with regards to the distortion of polyhedra, which we may simply indicate as the difference δ between the longest and the shortest distances in the polyhedron. The values for the *M*1 site in wöhlerite and "marianoite", 0.418 and 0.441 Å respectively, compare with the value found for the Nb site in niocalite (0.372 Å). Clearly lower values have been found for the *M*2 site in wöhlerite and "marianoite", 0.115 and 0.105 Å, respectively, which compare with the values found at other sites presenting a dominant Zr occupancy in minerals of the cuspidine family: the Zr site in låvenite (with some substitution by Nb): δ = 0.214 Å (Mellini 1981); the Zr site in hiortdahlite I: δ = 0.176 Å (Merlino & Perchiazzi 1985), in hiortdahlite II: δ = 0.092 Å (Merlino & Perchiazzi 1987), and in burpalite, δ = 0.035 Å (Merlino *et al.* 1990).

TABLE 3. BOND DISTANCES AND SITE DISTORTION AT THE *M*1 AND *M*2 SITES OF WÖHLERITE AND "MARIANOITE", AS WELL AS AT THE Nb AND Zr SITES OF NIOCALITE AND LÅVENITE, RESPECTIVELY

	wöhlerite	"marianoite"	Nb site in niocalite
*M*1	1.842 Å	1.828 Å	1.884 Å
	1.864	1.835	1.943
	1.995	1.987	1.950
	2.097	2.111	2.126
	2.141	2.154	2.131
	2.260	2.269	2.256
average	**2.033**	**2.031**	**2.048**
δ	**0.418**	**0.441**	**0.372**

	wöhlerite	"marianoite"	Zr site in låvenite
*M*2	2.046Å	2.055Å	2.010Å
	2.056	2.055	2.029
	2.075	2.068	2.035
	2.077	2.070	2.069
	2.088	2.074	2.129
	2.161	2.160	2.224
average	**2.084**	**2.080**	**2.083**
δ	**0.115**	**0.105**	**0.214**

Admittedly, we may find niobium compounds with smaller distortions at the Nb site and zirconium compounds with larger distortions at Zr site, and we agree with Chakhmouradian *et al.* (2008) that the distortion is controlled also by "electrostatic forces exerted by ions outside the nearest coordination sphere". It is exactly for this reason that we compare the behavior of Nb and Zr in the same class of compounds, presenting the same or a very similar structural arrangement. In all the minerals of the cuspidine group, the Zr sites present a definitely smaller distortion with respect to the Nb site in niocalite.

Bond-valence balance

Figure 1 shows that the regular alternation of Nb^{5+} and Na^{+} in the second "octahedral" column and Zr^{4+} and Ca^{2+} in the fourth column are the most appropriate to assure local equilibrium of charges. However, a reliable test to establish the actual distribution of cations at *M*1 and *M*2 sites requires a bond-valence calculation. Table 4 compares the results of bond-valence-balance calculations for the ordered (Nb at *M*1 and Zr at *M*2) and disordered ($Nb_{0.5}Zr_{0.5}$ at both sites) distributions for "marianoite" (at left), as well as for the ordered ($Nb_{0.8}Ti_{0.2}$ at *M*1 and Zr at *M*2) and the disordered ($Nb_{0.4}Ti_{0.1}Zr_{0.5}$ at both sites) distributions for wöhlerite. The comparison is made only for the anions involved in *M*1–O and *M*2–O bonds, as the other anions are not affected by the cationic distributions in *M*1 and *M*2 sites. The calculations have been made on the basis of the bond-valence parameters given by Brese & O'Keeffe (1991).

The bond-valence-balance calculations also unambiguously point to an ordered distribution of the cations in the two smallest octahedra of the structural arrangements of wöhlerite and "marianoite".

Thermal parameters

Finally, the behavior of the equivalent thermal parameters at the *M*1 and *M*2 sites in wöhlerite and "marianoite" is not as irrelevant in supporting our model of distribution as assumed by Chakhmouradian *et al.* (2008). In Figure 2, we present a plot of the equivalent thermal parameters for the Ca (Ca1, Ca2, Ca3, Ca4), Zr and Nb sites in wöhlerite as a function of the average distance in each polyhedron, as well as a similar plot for "marianoite". As expected, the equivalent thermal parameters regularly increase with increasing average bond-distance, with the marked exception of the equivalent thermal parameter for Nb, in keeping with our assumption of a 20% replacement of Nb by Ti at that site ["Ti^{4+} exhibits a smaller off-centre displacement; … we can expect a high equivalent thermal parameter for

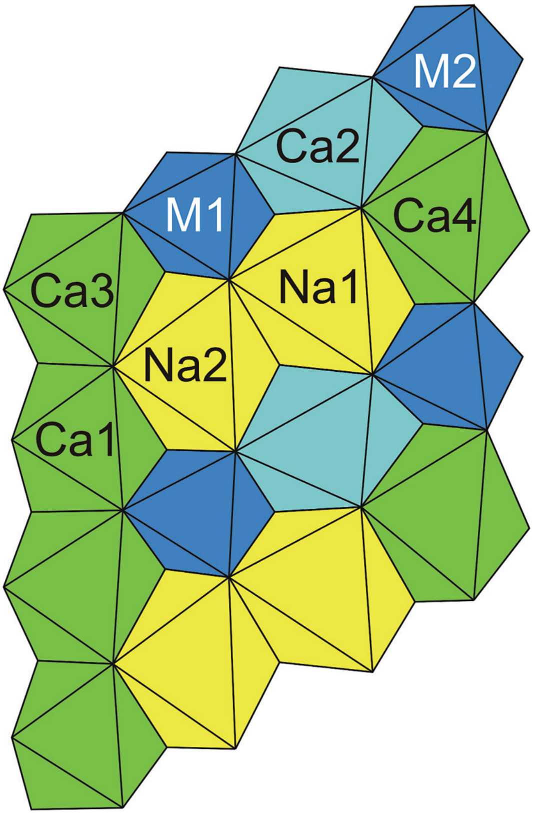

FIG. 1. Cation distribution in the "octahedral" walls of "marianoite". All the cationic environments are represented as octahedra, although Ca2 is seven-coordinated, and Ca4, Na1, Na2 are eight-coordinated.

the Nb site" (Mellini & Merlino 1979)]. The absence of such deviation from the plot for the point corresponding to the *M*1 site in "marianoite" ($B_{eq} = 0.53$ for *M*1, average bond-distance 2.031 Å; $B_{eq} = 0.73$ for *M*2, average bond-distance 2.080 Å) confirms the absence of relevant cation-mixing at the *M*1 and *M*2 sites, in accordance with our model of ordered distribution of Nb at *M*1 and Zr at *M*2.

CONCLUSION

It is evident that we may rephrase a concluding sentence by Chakhmouradian *et al.* (2008) as follows: "From the above discussion, it is clear that the partitioning of Nb and Zr between the two smallest octahedrally coordinated sites in wöhlerite and "marianoite" can be determined unambiguously." In fact, a given cation is characterized not only by its electron-density maximum, but also by its radius, its charge and its peculiar crystal-chemical behavior. Consequently, not only the X-ray-scattering power, but also the bond distances, the bond-valence balance, and the site distortion are experimental lines of evidence to be taken into due account. All those lines of evidence concurrently

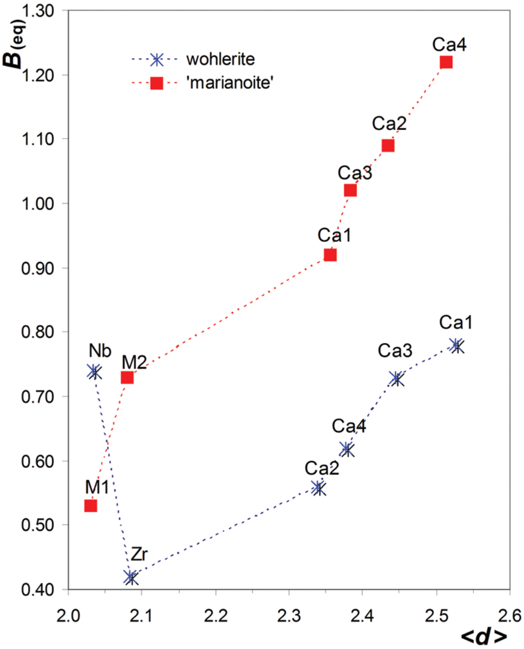

FIG. 2. Plot of B_{eq} versus the average bond-distances for cationic sites in wöhlerite and "marianoite".

TABLE 4. BOND-VALENCE-BALANCE CALCULATIONS FOR *M*1 AND *M*2 SITES IN MARIANOITE, AND Nb AND Zr SITES IN WÖHLERITE, FOR ORDERED AND DISORDERED DISTRIBUTIONS OF CATIONS

	"Marianoite"				Wöhlerite		
anion	O.D.	I.V.	D.D.	anion	O.D.	I.V.	D.D.
O5	1.893	2.00	1.907	O1	1.876	2.00	1.900
O4	2.047	2.00	2.066	O3	2.000	2.00	2.032
O3	1.993	2.00	2.014	O4	1.986	2.00	2.023
O8	1.894	2.00	1.870	O5	1.893	2.00	1.855
O7	1.986	2.00	1.966	O6	1.990	2.00	1.953
O10	1.957	2.00	1.939	O8	1.946	2.00	1.918
O6	2.049	2.00	2.025	O9	2.006	2.00	1.968
O11	2.017	2.00	1.992	O10	2.004	2.00	1.964
O12	1.941	2.00	1.946	O13	1.893	2.00	1.898
O17	1.946	2.00	1.991	O14	1.800	1.80*	1.867
O16	2.150	2.00	2.195	O16	2.088	2.00	2.159
$\Sigma\Delta^2$	0.059		0.077	$\Sigma\Delta^2$	0.049		0.084

O.D.: ordered distribution, I.V.: ideal value, D.D.: disordered distribution.
* As explained by Mellini & Merlino (1979), the occupancy of this anionic site is assumed to be ($O_{0.8}F_{0.2}$).

support, in the present case, our assumptions about cation partitioning in wöhlerite and "marianoite".

We are obviously aware that some limited substitution of Nb by Zr at the *M*1 site and of Zr by Nb at the *M*2 site is not only possible but also probable, but to a degree so as to keep Nb and Zr dominant at the *M*1 and *M*2 sites, respectively. In fact, in wöhlerite, the best agreement between calculated and observed bond-lengths may be obtained by assuming minor substitutions of Zr at the *M*1 site and of Nb at the *M*2 site: *M*1 ($Nb_{0.6}Ti_{0.2}Zr_{0.2}$) 2.027 Å (calc.), 2.033 Å (obs.); *M*2 ($Zr_{0.8}Nb_{0.2}$) 2.082 Å (calc.), 2.084 Å (obs.). Similar substitutions in "marianoite" result in the following calculated bond-distances: *M*1 ($Nb_{0.8}Zr_{0.2}$) 2.034 Å (calc.), 2.031 Å (obs.); *M*2 ($Zr_{0.8}Nb_{0.2}$) 2.082 Å (calc.), 2.080 Å (obs.).

On the other hand, it would be sufficient to have only a slight excess of Nb (for example 55% Nb) at site *M*1 to definitely rule out the possibility of Nb dominance at both *M*1 and *M*2 sites, which is the necessary condition for the definition of "marianoite" as a new mineral species.

It appears surprising that whereas they claim to proceed to a nomenclatural simplification, Chakhmouradian *et al.* (2008) start this claimed simplification by introducing an unnecessary new mineral name. Moreover, it is particularly disappointing that they criticize our work without any serious experimental evidence and relying only on groundless arguments.

The potential presently offered by synchrotron radiation sources allow one to distinguish isoelectronic cations through studies of anomalous scattering with X-ray radiation of appropriate wavelength. In the present case, the maximum difference in the scattering power of Zr and Nb is obtained at a wavelength λ of 0.6890 Å ($\Delta f' \approx -8.0$ for Zr; $\Delta f' \approx -2.3$ for Nb). The difference in the scattering power of the two cations should be sufficient to lead to an accurate "direct" refinement of occupancies at the *M*1 and *M*2 sites.

If Chakhmouradian *et al.* (2008) do need such additional proof to be convinced of the prevalent occupation of *M*1 and *M*2 sites by niobium and zirconium, respectively, we suggest that they carry out such an experiment, which, in our view, they should have undertaken before proceeding to the discreditation of our work.

Our final suggestion is addressed to the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association. Whenever the proposal of a new mineral is based on the discreditation of a preceding study, it would be proper to ask the authors of that study for comments and remarks. Fortunately, both authors in the present case are still alive, and they would have been glad to help the Commission in reaching its decision.

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