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

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General Comment

A systematic approach to the nomenclature of minerals showing (or potentially showing) an ordered distribution of cations over two or more topologically similar crystallographic sites is important for providing a consistent basis for the classification of minerals and interpretation of structural relations among similar minerals. Merlino & Mellini (2009) explore this theme in much detail in their comments on our description of the new mineral species *marianoite* (Chakhmouradian *et al*. 2008). The latter is related to wöhlerite, which was discovered in the Langesundsfjord area of Norway by Scheerer (1843, 1844) and studied structurally by Mellini & Merlino (1979). Numerous occurrences of wöhlerite in syenitic pegmatites throughout that area have been recognized, but its type locality remains unknown (G. Raade, pers. commun.). The provenance of the crystal studied by Mellini & Merlino (1979) is also unknown, because the cited location ("Brevig", p. 110) is actually situated outside of the Langesundsfjord pegmatitic area (see Fig. 1 in Raade 2008) and is merely a place where many local mineral dealers were stationed in the 1800s (G. Raade, pers. commun.). It is also important to note here that the chemical analysis of the "Brevig" wöhlerite performed by Mellini & Merlino (1979) is incomplete and for their purposes, they simply adopted the Nb and F values reported for samples from other unknown (*nota bene*) localities in the Langesundsfjord area by Brögger & Cleve (1890) and Tschernik (1909).

Irrespective of these serious problems with their structurally studied material, Merlino & Mellini (2009) challenge in their comments the validity of our findings and the mineral marianoite, which they mistakenly refer to as "marianoite" (*sic*), and make a number of misleading statements regarding our interpretation of the crystal chemistry of these minerals, which will be addressed below. First of all, we would like to emphasize here that marianoite was approved by majority vote (86.4% with none opposed) of the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA), and that the issues raised by our esteemed critics in their comments were brought to the attention of the Commission and discussed at length *prior* to the approval. Hence, marianoite is a valid mineral name and, as such, should not be enclosed in quotation marks.

Discussion

Unfortunately, in their comments, Merlino & Mellini (2009) misrepresent the key postulate of our work. They claim that "according to Chakhmouradian *et al*. (2008), zirconium and niobium are randomly distributed on the two sites" (*i.e*., octahedrally coordinated *M*1 and *M*2 sites in the crystal structure of marianoite). In fact, we make no such claim (the word "random" does not appear anywhere in our paper). One of the major conclusions of our work actually was 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" (Chakhmouradian *et al*. 2008, p. 1030). One should hope that experienced structural crystallographers would appreciate the difference between a random distribution of two cations over a pair of crystallographic sites and one where the exact proportion of these cations in either of the sites cannot be measured reliably.

Mellini & Merlino (1979) and Merlino & Mellini (2009) invoke calculated average bond-distances to support their model of complete Nb–Zr order at the *M* sites in the crystal structure of wöhlerite. They cite

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[§] *E-mail address*: chakhmou@cc.umanitoba.ca an allegedly superior result obtained with their model relative to a model based on a disordered distribution of Nb and Zr ($\Sigma\Delta^2 = 0.68 \times 10^{-3}$ and 1.33×10^{-3}, respectively). Using an ionic radius of 1.378 Å for oxygen (as recommended by Merlino & Mellini 2009), we obtain a result statistically identical to their "superior" model ($\Sigma\Delta^2 = 0.68 \times 10^{-3}$) with Nb and Zr distributed largely *at random* between the two sites: ($Zr_{0.45}Nb_{0.35}Ti_{0.2}$) at *M*1 and ($Zr_{0.55}Nb_{0.45}$) at *M*2.

Merlino & Mellini (2009) further criticize our reference to the NbO_6 polyhedron in $NaNbO_3$ to demonstrate that bond-length variations fail to provide convincing grounds for discriminating between Nb- and Zr-populated sites (Chakhmouradian *et al.* 2008, p. 1030). They state, "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 was 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." This statement is misleading, because it was Mellini & Merlino (1979) who chose $NaNbO_3$ as their case in point. We quote, "The Nb–oxygen distances are scattered from 1.842 to 2.260 Å... This means that Nb is not located in the centre of the octahedron, but displaced 0.23 Å from the centroid. Such a pattern of short and long distances is quite common for six-coordinated Nb^{5+} cation; for example, it was described by Sakowski-Cowley *et al.* (1969) for $NaNbO_3$ and by Choisnet *et al.* (1977) for $K_3Nb_3O_3B_2O_{12}$" (p. 119). In fact, nowhere in their discussion of bond-length variations in the *M*1 and *M*2 polyhedra do Mellini & Merlino (1979, p. 119-121) actually refer to other cuspidine-group minerals (Merlino & Mellini 2009, p. 1277). Hence, it seems entirely appropriate that Chakhmouradian *et al.* (2008) used the same example (*i.e.*, $NaNbO_3$) to illustrate the unreliability of bond-length variations for accurate assessment of site occupancies.

In their discussion of the measured equivalent thermal parameters in wöhlerite, Mellini & Merlino (1979) surmise that the large deviation of the equivalent thermal parameter for the *M*1 site from the expected value (see Fig. 2 in Merlino & Mellini 2009) is in accord with a 20% substitution of Ti^{4+}, which shows "a smaller off-centre displacement" relative to Nb^{5+} (p. 119). Following the same logic, we can counter-argue that the observed deviation is more likely to be due to significant substitution of Nb^{5+} by Zr^{4+}, which is larger than Nb^{5+} and better explains the significant positive offset of the $B_{eq}(M1)$ value from the trend constructed on the basis of the experimentally determined cation–anion distances (Fig. 2 in Merlino & Mellini 2009). Overall, however, we are convinced that because the measured thermal parameters in the *M*1 and *M*2 sites behave very differently in the crystal structures of wöhlerite and marianoite, these parameters should not be used to support any cation-assignment model (*i.e.*, neither theirs nor the disordered one). Indeed, if the two minerals were "actually identical" (Merlino & Mellini 2009, p. 1275), should they not be expected to exhibit the same trend of B_{eq} values?

Finally, Merlino & Mellini (2009) place inordinate emphasis on the distribution of bond-valence values in the crystal structure of wöhlerite, proposing to be able to pinpoint the location of Zr, Nb and F in that structure on the basis of their calculated bond-valence values (Table 5 in Mellini & Merlino 1979). It is important to note here that neither Nb nor F contents in their sample were determined analytically (*ibid.*, p. 111) and, hence, in their analysis, Mellini & Merlino (2009) are actually comparing the values derived from their single-crystal X-ray data with the values "expected" from... well, the same X-ray data. Let us assume for the moment that the results of 100-year-old chemical analyses obtained for wöhlerite from unknown localities in the Langesundsfjord area (Brögger & Cleve 1890, Tschernik 1909) somehow apply to the "Brevig" sample studied by Mellini & Merlino (1979). Given that neither the absolute amount nor the structural distribution of F in the sample of Mellini & Merlino (1979) are known precisely, we performed bond-valence calculations without constraining the occupancy of the O14 site first for the completely ordered structural model of Mellini & Merlino (1979), and then assuming a random distribution of Zr, Nb and Ti over the *M*1 and *M*2 sites. From the results compared in Table 1, it follows that the *disordered* model gives a better match with the actual distribution of anion valences. As we have stressed before, these numbers do not necessarily imply that Zr and Nb are distributed in the crystal structure of

TABLE 1. BOND-VALENCE CALCULATIONS[‡] (UNADJUSTED) FOR THE *M*1 AND *M*2 SITES IN WÖHLERITE

Site	ordered model	ideal	disordered model[†]
O1	1.927	2.000	1.943
O3	2.037	2.000	2.059
O4	2.032	2.000	2.056
O5	1.922	2.000	1.896
O6	2.013	2.000	1.988
O8	1.974	2.000	1.953
O9	2.015	2.000	1.989
O10	2.030	2.000	2.002
O13	1.868	2.000	1.872
O14	1.779	2.000	1.826
O16	2.080	2.000	2.129
$\Sigma\Delta^2$	0.088		0.086

[‡] The calculations were performed using the bond-valence parameters of Brown & Altermatt (1985) and Tytko *et al.* (1999).

[†] The structural model based on a completely disordered distribution of Zr and Nb over the *M*1 and *M*2 sites is not endorsed in any way by the authors of the present contribution. It simply serves to illustrate the limitations of the approach of Mellini & Merlino (1979) to the interpretation of structural data.

wöhlerite completely at random; they simply indicate that the occupancy of the two sites *cannot be determined accurately* because the two elements have very similar X-ray scattering characteristics, and the distribution of bond valences is affected by factors other than site occupancies. For example, the sum of bond valences for the Nb site in niocalite, a mineral structurally related to wöhlerite but containing negligible Zr, is 4.44 (Mellini 1982), *i.e.* 11% smaller than the expected value. Does this relatively large discrepancy mean that the structure of niocalite was determined incorrectly? Of course, not! It simply serves to illustrate the limitations of bond-valence analysis. It is now well known that, for a given atom, the budget of bond valences can be affected significantly by weak interactions with atoms outside of its first coordination sphere, which may contribute as much as 10% toward the bond-valence sum (*e.g.*, Adams 2001). A detailed discussion of this and other intricacies of bond-valence analysis is beyond the scope of the present work; interested readers are referred to Brown (2009).

CONCLUSION

To summarize, the objective of our work on marianoite was *not* to undermine the importance of structural analysis for mineralogical research, much less to "discredit" the work of Mellini & Merlino (1979). As academics, we are both entitled and obligated to share our findings and, where necessary, inform the reader about limitations of the techniques we use, even if these findings happen to disagree with someone else's interpretations. In the present case of marianoite *versus* Nb-rich wöhlerite, the overwhelming approval of the former mineral by CNMNC IMA is a convincing demonstration that there is much more to our contribution than just "groundless arguments".

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