

Comments on: Strunz and Nickel: “Pseudosinhalite is a structural isotype of chondrodite”

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ABSTRACT

Pseudosinhalite, $Mg_2Al_3O[BO_4]_2(OH)$, can, on chemical grounds, be regarded as a member of a polysomatic series consisting of two modules of the forsterite analogue sinhalite, $MgAl[BO_4]$, and one module of $AlO(OH)$. However, in contrast to the isostructural polysomatic humite series with five members including forsterite, experiments suggest that there are no synthetic $MgAl$ -analogues for the members norbergite, humite, and clinohumite.

We wish to congratulate H. Strunz and E. Nickel on their finding that our new hydrous $MgAl$ -borate mineral pseudosinhalite is a structural analogue of the silicate mineral chondrodite. Because the latter belongs to the polysomatic series forsterite-clinohumite, the question of more borate isotypes arose (Strunz and Nickel 2000, Table 1). Although a synthetic anhydrous Fe borate was mentioned as an isotype of norbergite, question marks were shown for humite and clinohumite, but their possible finding would not be deemed as surprising. In particular, the question remains as to whether or not there may be other $MgAl$ -borates in addition to sinhalite and pseudosinhalite with structures analogous to the remaining three members of the clinohumite series. The experimental data on pseudosinhalite presented by Daniels et al. (1997) allow a careful answer to this question. Moreover, on the basis of their structural data, the polysomatic nature of pseudosinhalite can be tested.

The polysomatic nature of the humite group of minerals was proposed by Deer et al. 1962) as an interlayering of modules of forsterite, $Mg_2[SiO_4]$, and brucite-sellaite, $Mg(OH,F)_2$, in various proportions, with the general chemical formula $Mg(OH,F)_2 \cdot nMg_2[SiO_4]$. For the four members, norbergite, chondrodite, humite, and clinohumite, $n = 1, 2, 3,$ and $4,$ respectively. The crystal structures of these minerals were described by Ribbe et al. (1968), who pointed out that the simple picture of module interlayering as given above is structurally incorrect, because the so-called “layers” actually share common cations and anions with the neighboring layers. Ribbe et al. (1968) gave the general formula as $Mg_{2x}Si_{x-1}O_{4x-4}(OH,F)_4$ with $x = 3, 5, 7, 9.$ Nevertheless, purely on chemical grounds, the polysomatic formula is still useful (Deer et al. 1982).

With this background, two main questions are addressed in the following for the $MgAl$ -borates: (1) Can pseudosinhalite also be regarded as a sort of “composite” structure consisting of two chemically defined modules? (2) Do any other members of such polysomatic series exist in the system $MgO-Al_2O_3-B_2O_3-H_2O,$ likely as in the Mg -silicate case?

QUESTION 1

Simply from its chemical formula $Mg_2Al_3O[BO_4]_2(OH)$, it can be seen that pseudosinhalite may indeed be split up formally into two units of sinhalite, $MgAl[BO_4]$, the mineral isostructural to forsterite, and one unit of diaspore (or boehmite), $AlO(OH)$. Looking at the crystal structure of pseudosinhalite (Daniels et al. 1997), the scheme used by Deer et al. (1982, Fig. 203) for chondrodite can indeed be adopted for pseudosinhalite as well (Fig. 1): two layers of sinhalite are followed by one of diaspore composition (disregarding any kinship to the diaspore structure). Whereas only Mg occupies the octahedra of the chondrodite structure, both Mg and Al fill these positions in the pseudosinhalite structure. In addition, Si in the tetrahedral sites is replaced by B . The protons present in pseudosinhalite form hydrogen bonds of exceptional strength according to the IR-spectrum (Daniels et al. 1997). These protons, which belong formally and geometrically to the $AlO(OH)$ layers, are bonded to a class of O atoms with crystal-chemical properties different from all other O atoms in the structure because they are not part of the BO_4 -tetrahedra. No data are available as yet on the type of hydrogen bonding in pure synthetic chondrodite-OH (Wunder 1998). At any rate, if chondrodite can be described chemically as consisting of layers with distinct chemical compositions,

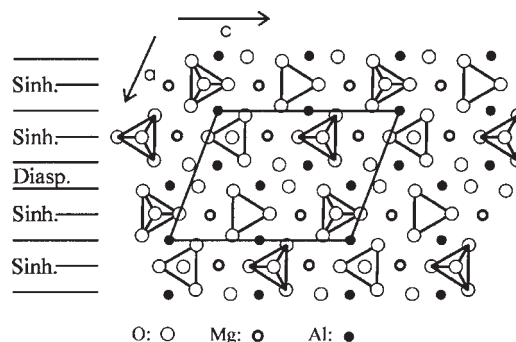


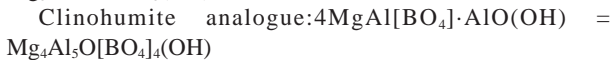
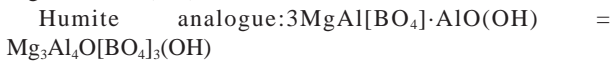
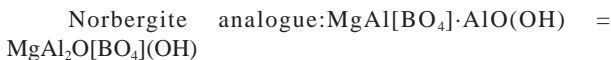
FIGURE 1. Projection of the pseudosinhalite crystal structure along [010]. The Mg - Al distribution is taken from Daniels et al. (1997). The positions of BO_4 -tetrahedra are indicated, but the B atoms themselves are not shown. On the left-hand side of the figure, the chemical layers akin to sinhalite and diaspore are indicated.

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then the same can be said about pseudosinhalite, and the same discussion about the usefulness and justification (Ribbe et al., 1968) of such a description can be applied to the pseudosinhalite structure as well. The structural model of Ribbe et al. (1968) also can be used for the borate system and leads to the general formula $Mg_{x-1}Al_{x-1}Al_2B_{x-1}O_{4x-4}(OOH)_2$, again with $x = 3, 5, 7, 9$ (pseudosinhalite having $x = 5$).

QUESTION 2

Other hypothetical members of a polysomatic series analogous to the humite-group minerals, but consisting of the chemical modules sinhalite and diaspore, would be the following:



The general formula of this hypothetical group expressing only the possible chemical variations would be $AlOOH\text{-}mMgAl[BO_4]$. These theoretical compositions of the relevant chemical system $MgO\text{-}Al_2O_3\text{-}B_2O_3\text{-}H_2O$ lie along the join sinhalite-diaspore just like pseudosinhalite (Daniels et al. 1997, Fig. 1), which is shown here as a binary projection in Figure 2.

Daniels et al. (1997) reported synthesis runs performed on two different bulk compositions along this join, one that of pseudosinhalite, the other with a ratio $MgO:Al_2O_3:B_2O_3 = 2:3:1$ (see Fig. 2). Whereas the pseudosinhalite runs either yielded this phase only, or mixtures of pseudosinhalite + sinhalite + corundum, or of sinhalite + corundum only, that on the 2:3:1-composition gave pseudosinhalite + corundum. These results indicate that no other crystalline phases could be synthesized under the conditions chosen: the assemblages pseudosinhalite + corundum, pseudosinhalite + sinhalite, and sinhalite + corundum preclude, in the presence of a hydrous fluid, the existence of any of the additional polysomatic borate phases shown in Figure 2. Daniels et al. (1997, Fig. 8) also reported the result of one run on sinhalite composition, which yielded the assemblage pseudosinhalite + szaibelyite, $MgBO_2(OH)$. Because szaibelyite plots along the left-hand extension of Figure 2, this result provides further support for the absence of humite- and clinohumite analogues. Although all these data do not repre-

sent conclusive evidence for the complete instability of other hydrous MgAl-borate phases under any physical-chemical condition, this may well be so.

This discussion leads us to a final question as to whether or not there may be reasons of crystal chemistry that favor the formation of the chondrodite analogue in the MgAl-borate system, but prevent other structures of a polysomatic series from existing. One reason might be the fact that there are two different octahedral cations involved in the borate phase, but only one (Mg) in the silicates, thus leading to varying ratios of Mg and Al over the hypothetical polysomatic series (see theoretical formulae above). Another reason might be the different roles for F in the two structural isotypes. Whereas all Ti-free natural chondrodites and other natural humite-group minerals contain substantial amounts of F, pseudosinhalite is free of this element both in nature (Schreyer et al. 1998) and experiment (Daniels et al. 1997). However, because hydroxyl analogues of the humite-group phases become stable only at high pressures (e.g., Wunder 1998), it is clear that F has a stabilizing effect on these minerals. Fluorine really has the role of an anion in the humite structures, whereas in pseudosinhalite, the H acts as a third cation in addition to Mg and Al causing the strong hydrogen bonding. A very thorough and detailed theoretical investigation employing advanced quantum chemical methods, as well as clarification of the role of H in synthetic high-pressure chondrodite-OH and other hydroxyl humites would, therefore, be necessary to shed light on the above question.

In summary, there are no indications that hydrous MgAl-borates with structures analogous to the humite-group silicates exist, except for the chondrodite analogue pseudosinhalite (Strunz and Nickel 2000). An even more negative experience was recently reported by Chopin and Brunet (2000) on the hydrous Mg-phosphates: although one polymorph of the phase $Mg_3(PO_4)_2$ exhibits a forsterite-type structure, and although there are numerous hydrous Mg-phosphates in the requisite chemical system, none of them has a humite-type structure. Even direct attempts by those authors to synthesize analogues of the humite family were unsuccessful.

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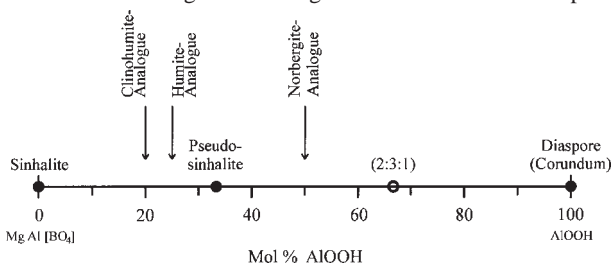


FIGURE 2. Chemical compositions of hypothetical (arrows) and existing (solid dots) phases along the join $MgAl[BO_4]\text{-}AlO(OH)$ (sinhalite-diaspore). The four intermediate phases would form a polysomatic series analogous to the humite group of minerals. The open circle (2:3:1) indicates a bulk composition studied experimentally by Daniels et al. (1997).