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Topological comparison between high-pressure borates and ambient-pressure silicates

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In the context of our investigations into high-pressure / high-temperature synthesis of new rare-earth oxoborates, we were able to discover several new high-pressure polymorphs of known compositions and additionally new compositions, whose successful syntheses were indispensably based on the "pressure" parameter. For example, all attempts to produce rare-earth borates with the ratio $RE_2O_3 : B_2O_3 = 2: 3, 1: 2$, and $3: 5$ under normal-pressure conditions were in vain. In contrast, the corresponding multianvil high-pressure experiments [1] led in most cases to phase pure rare-earth borates $RE_4B_6O_{15}$ (RE = Dy, Ho) [2], β-$RE_2B_4O_9$ (RE = Sm-Ho) [3], β-$RE_2B_4O_9$ (RE = Dy, Gd) [4], and $RE_3B_5O_{12}$ (RE = Tm-Lu) [5].
Due to the pressure-coordination rule, extreme synthetic conditions of 10 GPa favour structures, in which boron is exclusively coordinated to four oxygen atoms. Therewith, structural similarities with silicate chemistry can be assumed. In fact, we found several examples of beryllosilicates, in which the topology of the tetrahedral (Be,SiO_4)-network corresponds to the arrangement of BO_4-tetrahedra in our new high-pressure borates. E.g., the crystal structures of the former mentioned high-pressure borates $RE_3B_5O_{12}$ (RE = Tm-Lu) [5] are homeotype to the beryllosilicate mineral semenovite ((Fe^{2+}, Mn, Zn, Ti)RE_2Na_{0-2}(Ca, Na)$_8$(Si, Be)$_{20}$(O, OH, F)$_{48}$) [6]. Recently, Krivovichev *et al.* reported about the crystal structure of clinobarylite $BaBe_2Si_2O_7$ [7], which is isotypic to SrB_4O_7 and the high-pressure polymorphs β-CaB_4O_7 and β-HgB_4O_7. Additionally, we discovered a new ternary borate in the system Hf-B-O with the composition HfB_2O_5 ($P2_1/c$, a = 438.48(9), b = 690.60(2), c = 897.60(2) pm, β = 90.76°, $wR2$ = 0.0502 (all data), 1186 F^2 values, 74 variable parameters). This compound represents the first crystalline hafniumborate exhibiting a structure, which is homeotype to minerals crystallizing in the gadolinite-type structure (e.g. $NiYb_2Be_2Si_2O_{10}$) [8].
The talk will introduce the topological similarities and differences between high-pressure borates and ambient-pressure silicates.

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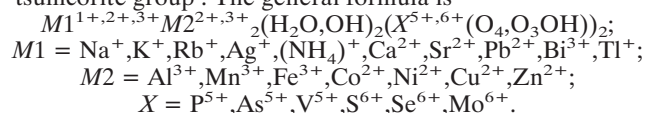## Hydrogen bonds controlling the structure type

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The roles of hydrogen atoms controlling variants of crystal structures have been overseen often. Two examples exhibiting complex order phenomena are presented.
About 30 natural and synthetic compounds belong to the 'tsumcorite group'. The general formula is
$M1^{1+,2+,3+}M2^{2+,3+}{}_2(H_2O,OH)_2(X^{5+,6+}(O_4,O_3OH))_2$;
$M1$ = $Na^+,K^+,Rb^+,Ag^+,(NH_4)^+,Ca^{2+},Sr^{2+},Pb^{2+},Bi^{3+},Tl^+$;
$M2$ = $Al^{3+},Mn^{3+},Fe^{3+},Co^{2+},Ni^{2+},Cu^{2+},Zn^{2+}$;
X = $P^{5+},As^{5+},V^{5+},S^{6+},Se^{6+},Mo^{6+}$.
For each of the cation sites $M1$, $M2$ and X at least two different valences are possible; the coupled exchange at these cation positions and adjusting the ratio OH:H_2O ensures electroneutrality. Most members are monoclinic forming H_3O_2 groups, *i.e.*, a strong symmetry-restricted hydrogen bond between two OH groups linked by a centre of inversion ('tsumcorite type'; C centred cell with Z = 2). Two structure variants with lower (triclinic) symmetry are caused by distinct crystal-chemical requirements: In the 'helmutwinklerite type' (P centred with Z = 4) two H_2O molecules per formula unit require an avoidance of the symmetry-restricted hydrogen bond. Secondly, *di*valent copper besides *tri*valent iron ions require a mechanism for individual environments at their $M2$ sites; the inversion centres are maintained ('gartrellite type'; P centred with Z = 1). Hydrothermal syntheses produced the new compound $SrCo_2(AsO_4)(OH)(AsO_3OH)\_H_2O$ which represents the first proof of (partial) protonated arsenate groups in this series of compounds: 'Sr-Co type' (P centred monoclinic with Z = 4). The As-atom site splits into two crystallographically independent sites going along with the formation of $(AsO_4)^{3-}$ besides $(AsO_3OH)^{2-}$ groups. The symmetry restriction of the hydrogen bond is given up: the former equivalent oxygen atoms split into one representing a H_2O molecule whereas the other one belongs to a hydroxyl group.
A further complex variation of a parental structure is verified in the triclinic $MHXO_4$ compounds ($CaHPO_4$ - monetite, $CaHAsO_4$ - weilite, α-$NaHSO_4$, α-$SrHPO_4$, $HgHPO_4$, and $SrHAsO_4$). The location of the M atoms and XO_4 tetrahedra is roughly the same. There are three topologically distinct hydrogen bonds: (*i*) One hydrogen atom is located close to an inversion centre forming a symmetry-restricted hydrogen bond. (*ii*) A further short hydrogen bond has the donor and acceptor atoms not related by (average) space-group symmetry. However, the direction of the hydrogen bond (OH dipole) may be inverted and the donor and acceptor function of the oxygen atoms belonging to this hydrogen bond is interchanged. (*iii*) In total four O atoms are involved into the formation of the third hydrogen bond; their interactions with respect to the H atom differ. The hydrogen bond is either in or close to an edge in the MO_8 coordination polyhedron; it may be bifurcated. In $Sr(AsO_3OH)$ a super-structure avoids symmetry centres in the vicinity of all the H atoms; all H bonds have distinct donor and acceptor atoms. Complete order of the H atoms in $SrHAsO_4$ and the low-temperature modification of monetite cause mono-protonated anion groups. In the other cases $[XO_2(OH)_2]$ groups are necessarily formed besides $[XO_3(OH)]$ and $[XO_4]$ groups.