

**08.1-17 ALUMINIUM: WHEN IS IT LIKE SILICON?**

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The ready substitution of aluminium for silicon in a variety of silicates, especially framework silicates, suggests the possibility of producing aluminium analogues of silicates. Framework aluminates such as the so-called "stuffed silica" structures typified by  $BaAl_2O_4$  have been known for a long time. All -aluminium analogues of sodalite have been prepared, and a few other framework aluminates are known; there are also ring and sheet aluminates. The structures of these are compared with those of similar silicates.

The survey of aluminium crystal chemistry is generalised to other oxygen - containing compounds (aluminates, mixed oxides and oxysalts). Aluminium, in addition to carrying a lower formal charge than silicon, adopts octahedral coordination much more readily, and this leads to many structural differences. Octahedral coordination is favoured by the presence of electro-negative elements such as phosphorus and sulphur; a similar, but much less pronounced, tendency is seen with silicon. Oxygen present as hydroxyl ion also favours octahedral coordination. The presence of electropositive elements, on the other hand, generally favours tetrahedral coordination of the aluminium.

An attempt is made to put this on a quantitative basis, by correlating the coordination number of the aluminium with the basicity of the oxygen atoms in the structure. The significance of the 'aluminium avoidance' rule in zeolites and feldspars (Loewenstein's rule) is also considered from this viewpoint.

isolated ring polyanions and, finally, by lamellar and framework structures.

Among the borates with large values of N-factor, the tendency to polymerization increases with the decrease of the cation size. The increase in the cation charge assists in weakening the polycondensation of the B triangles and tetrahedra as well as preference of tetrahedral coordination of boron atoms. The structure stability of borates with weak monocharged and large bivalent cations is secured by delocalization and decrease in the formal specific charge of an anion by its polymerization. Stability of BO-anions loses its decisive role in the case of cations with relatively large charges which are able to form around them stable coordination polyhedra usually forming the basis of the structure. Therefore not only isolated B triangles but also tetrahedra with a large negative charge are widespread in such structures.

Among the anhydrous borates the isostructural series and isomorphism are widespread both between the cations and anions, as well as the polymorphism of BO radicals. Metaborate radical  $[BO_2]_n$  (with n from 1 to 6) occurs in

34 island, chain, ribbon, lamellar and framework compounds. Some of their representatives have 2-3 and even 4 modifications. The triangle coordination of boron is regularly modified by the tetrahedral one as the degree of polymerization of a radical increases. Owing to their size, polyanions of the  $[BO_2]_n$  (n = 1 and 2),

$[B_3O_5]$  and  $[B_8O_{13}]$  type occupy 2-4 locations.

**08.1-18 STRUCTURAL ELEMENTS OF ANIONS AND POLYANIONS OF CRYSTALLINE ANHYDROUS BORATES.** By N.I. Leonyuk and L.I. Leonyuk, Geology Faculty of M.V. Lomonosov Moscow State University, Moscow, USSR.

Forty-four various anions and polyanions were selected from 342 borates, boron silicates and boron aluminates with known structures. Three types of structural elements are suggested as distinguishable among them. They differ in composition, the level of complexity, prevalence and informativity.

1. "Elementary" units (e.u.). They are triangles and tetrahedra.
2. Combined basic structural units (c.u.). Each of them consists of 2-6 e.u. united preferentially into single or double rings. In crystal structures of anhydrous borates they exist in isolated state or form chains, layers, three-dimensional networks (frameworks).
3. Complete radicals of polyanions (c.r.). Each one is built of 2-9 e.u. It may include more than one c.u. and may, apart from the latter, have additional e.u. - triangles and tetrahedra. The constituents of this category are complete repeated fragments of polyanions equal or multiple in composition to anionic parts of the structural formula of a compound. C.u. and c.r. are most varied in the structures of framework and lamellar borates. Three selected groups of structural elements characterize completely enough the crystal chemistry of these specific compounds.

Comparison between borate structures with the cations of the same name and different ratios  $N=N_M:N_B$  (i.e. different degree of acidity) has clearly demonstrated a general tendency of the BO-radical polymerization degree to increase with decreasing N-factor. Structures with isolated e.u. (anions) are replaced by borates with isolated pyro groups, then by structures with chain or

**08.1-19 THE WATER MOLECULES IN THE CRYSTALLINE HYDRATES STUDIED BY NEUTRON DIFFRACTION.** By G. Chiari and G. Ferraris, Istituto di Mineralogia, Cristallografia e Geochimica, Università, Via San Massimo 22, 10123 Torino, Italy.

A survey of the geometry and environment of water molecules in crystalline hydrates is presented. Histograms and correlation analyses are based on 97 crystal structures studied by neutron diffraction and include data from 183 water molecules; these are divided according to the nature of the hydrogen bond acceptors and of the coordinated cations. Cases of multiple hydrogen bonds are also analyzed and discussed. The widening of the H-W-H angle, with respect to the gas phase, is correlated both to the A-W-A angle and to the strength of the donated hydrogen bonds. The value of the H-W-H angle has a greater influence on the type of coordination than the lone-pairs on the oxygen atom. The length of the W-H bond which, on average, is shorter than in the gas phase, is correlated to the strength of the hydrogen bond, and to the nature of the acceptor as well as to the type of coordination.