

# THE DISTRIBUTION OF ALUMINUM IN THE TETRAHEDRA OF SILICATES AND ALUMINATES

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## ABSTRACT

In crystals of silicates and aluminates the distribution of aluminum in the centers of tetrahedra is not entirely at random, but must obey certain restrictions not easily understood on the basis of the Pauling electrostatic valence rule. Whenever two tetrahedra are linked by one oxygen bridge, the center of only one of them can be occupied by aluminum; the other center must be occupied by silicon, or another small ion of electrovalence four or more, e.g. phosphorus. Likewise, whenever two aluminum ions are neighbours to the same oxygen anion, at least one of them must have a coordination number larger than four, that is, five or six, towards oxygen. These rules explain the maximum substitution of 50% of the silicon in three-dimensional frameworks and plane networks of tetrahedra by aluminum. For 50% substitution, rigorous alternation between silicon and aluminum tetrahedra becomes necessary; this explains the experimental fact that the unit cell of anorthite has double the size of that of albite. Agreement of several known structures with these rules is shown. One exception is explained.

## INTRODUCTION

One of the most important features of the modern theory of silicates is the double rôle of aluminum, which can substitute for silicon in tetrahedra, and, on the other hand, function as an independent cation with coordination number five or six towards oxygen. Substitution of aluminum for silicon in tetrahedra was formerly considered to be entirely random and of infinite extent, and this view is presented even in modern text-books, e.g. by Evans (1). Although it was shown by Machatschki (2) in the structure of haüynite, and by Barth (3) in the structure of microcline, that at least in some cases the substitution of aluminum for silicon is not a random one, random substitution as a rule with possible exceptions was accepted by most authors. Thus, when the difference in the size of the unit cells of albite and anorthite was found by Taylor, Darbyshire and Strunz (4), it was attributed to a possible different coordination around the sodium and calcium ions, and not to a difference in the distribution of aluminum ions in the centers of tetrahedra. Also the well-known fact that in all known cases of substitution of silicon by aluminum in condensed tetrahedra the maximum substitution is 50% seems so far not to have been duly accounted for or explained. It clearly indicates alternation of silicon and tetrahedral aluminum positions.

## THE OXYGEN BRIDGES

The Pauling electrostatic valence rule does not explain why an oxygen bridge between aluminum tetrahedra should be excluded. In fact, it

would attribute to the oxygen one and a half electrostatic bonds, leaving one half to be satisfied by some other cation. The third of Pauling's rules (5) is more helpful in making the restriction comprehensible: it expresses the tendency of polyhedra around cations with small coordination number not to share elements with each other. Reciprocally, if elements are shared, but alternative structures with higher coordination numbers are possible, these should have higher stability. The condition that this effect is especially large when the radius ratio approaches the lower limit of stability of the polyhedron is clearly satisfied for aluminum with tetrahedral coordination. This effect of the radius ratio is particularly important for understanding the possibilities of existence of oxygen bridges between tetrahedra, even under conditions where the electrostatic valence rule is not satisfied. Thus, phosphate tetrahedra condense in pyrophosphates and metaphosphates, and also the anhydride  $P_4O_{10}$ , consists of four condensed tetrahedra, linked by oxygen atoms to which two and a half electrostatic bonds must be attributed. Sulfate tetrahedra condense in pyrosulfates, and probably in one of the forms of the anhydride, and in this case three electrostatic bonds must be attributed to the oxygen bridge. In perchloric anhydride,  $Cl_2O_7$ , three and one half electrostatic bonds pertain to the oxygen linking the tetrahedra. In these cases, the cations become successively smaller from aluminum to silicon and phosphorus, and then remain substantially of the same size.

In the structure found by Keggin (6) for phosphotungstic acid, subsequently established also for silicotungstic, borotungstic and metatungstic acid, four oxygen atoms link the central tetrahedron of the anion to three tungsten octahedra condensed in these same oxygens. The electrostatic valence bonds that must be attributed to these oxygen anions are respectively three and one half for metatungstic, three and three quarters for borotungstic, four for silicotungstic, and four and one quarter for phosphotungstic acid. Here, clearly, the limit of stability is reached; no sulphotungstic acid of analogous structure, though formally possible, is known. In all these cases, the radius ratio permits easy accommodation of the cations in the anion polyhedra, and where two possible numbers of coordination exist, the higher one is preferred; thus, boron is surrounded by a tetrahedron, not a triangle; hydrogen in the central tetrahedron has its maximum coordination of two; and hexavalent tungsten has its maximum coordination of six towards oxygen. These enhanced numbers of coordination account for the stability of the bridges, and electrostatic valence becomes of minor importance, since neutrality of the whole is maintained.

Similarly, the oxygen bridge between two aluminum ions has stability only when at least one of them has the enhanced coordination of five

or six, and, as a consequence, no two aluminum ions can occupy the centers of tetrahedra linked by one oxygen. Also in this case, it is of no consequence that electrostatic valence seems not to exclude the possibility of neighboring aluminum tetrahedra. The unfavorable radius ratio determines the instability of such a configuration.

The contradiction between the third Pauling rule and the electrostatic valence rule in its application to elements shared by anion polyhedra is only apparent. In reality, it must be assumed that in polyhedra with enhanced number of coordination the central atom or cation has a certain freedom of position and does not contact simultaneously all the surrounding anions. If one of these is shared with a polyhedron around another cation, the cation with enhanced number of coordination will be displaced by repulsion from the other cation, increasing its distance from the bridge anion, and thus weakening the electrostatic bond.

#### STRUCTURES WITH ALUMINUM OF FOUR AND FIVE OR SIX COORDINATION TOWARDS OXYGEN

In the structure of  $12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$ , investigated by Büssem and Eitel (7), less than half of the aluminum ions occupy the centers of tetrahedra, the others have higher, probably five, coordination towards oxygen. In corundum,  $\text{Al}_2\text{O}_3$ , the aluminum occupies the centers of octahedra, while the metastable  $\text{Al}_2\text{O}_3$ , investigated by Hägg and Söderholm (8, 9), has a defective spinel structure, with alternating tetrahedral and octahedral positions and some vacant sites. No known structure of  $\text{Al}_2\text{O}_3$  contains an excess of tetrahedral cations, or only such cations.

Only tetrahedral aluminum ions are, however, found in  $\text{KAlO}_2$ , investigated by Barth (10). This compound has a cristobalite structure, with potassium ions localized in the space between twelve oxygen anions. No alternative structure with coordination number of aluminum higher than four seems to be geometrically possible. This compound also does not conform strictly to the Pauling rules: the polyhedra around potassium share faces with each other, and with the tetrahedra around aluminum. The great distance between potassium and oxygen, 3.19 Å, permitting easy accommodation of the potassium ion in the oxygen polyhedron, offers an explanation for this exception to the rules.

#### STRUCTURES OF SILICATES

In kyanite,  $\text{Al}_2\text{SiO}_5$ , aluminum has sixfold coordination towards oxygen, silicon fourfold coordination. The structure, determined by Náray-Szabó, Taylor and Jackson (11), contains isolated silicon tetrahedra and oxygen anions. In andalusite, as determined by Taylor (12), coordination of aluminum is fivefold, of silicon fourfold. In sillimanite, investigated

by Taylor (13), half of the aluminum atoms occupy centers of octahedra, the other half centers of tetrahedra condensed with alternating silicon tetrahedra. The rational formula is  $\text{Al}(\text{AlSiO}_6)$ . The structure of mullite,  $\text{Al}_6\text{Si}_2\text{O}_{13}$ , also investigated by Taylor, is similar, but not identical. Its formula suggests it to be possibly, but not necessarily, an exception to the established rule.

In sheet structures of aluminum and silicon tetrahedra, maximum substitution of silicon by aluminum is 50%. This maximum is attained in the calcium micas, e.g. margarite,  $\text{CaAl}_2(\text{OH},\text{F})_2(\text{Al}_2\text{Si}_2\text{O}_{10})$ .

In three-dimensional frameworks of tetrahedra, 50% substitution of silicon by aluminum occurs in haüynite,  $\text{Na}_2\text{Ca}_4(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_2$ , the structure of which was determined by Machatschki (2), and in anorthite,  $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ , investigated by Taylor, Darbyshire and Strunz (4). In haüynite, alternation between silicon and aluminum tetrahedra was determined, and since the anorthite structure is very similar, it should also contain alternating silicon and aluminum tetrahedra. This explains why the anorthite unit cell has double the size of the albite cell. Albite,  $\text{Na}(\text{AlSi}_3\text{O}_8)$ , must be considered a defect structure in which no difference in the positions of aluminum and silicon can be detected. This defectiveness does not exist in anorthite. In spite of the difference in the size of the unit cell, the two minerals must be considered isomorphous. In the compositions with more than 50% anorthite, half of the positions in the centers of tetrahedra become prohibited for aluminum, which distributes statistically over the other half. The structure is still a defective one, for the aluminum positions are in part occupied by silicon; but this should be considered rather a substitution of aluminum of anorthite by silicon than of silicon by aluminum. In pure anorthite, no defectiveness of this type occurs, and the intensities of *x*-ray reflections due to the double cell become maximal.

#### CONCLUSIONS

The Pauling electrostatic valence rule admits exceptions for anions shared by polyhedra with enhanced number of coordination. The reason for these exceptions is the influence of the radius ratio upon the stability of structures, accounted for in the third of Pauling's rules. For the same reason, anion bridges between polyhedra with lowest possible number of coordination, though formally possible according to the electrostatic valence rule, must be expected to be unstable whenever alternative structures with higher numbers of coordination in a part of the polyhedra are possible. Substitution of aluminum for silicon ions in silicates is therefore not an entirely random one.

Since non-random distribution of aluminum atoms in the centers of tetrahedra explains the difference in the size of the unit cells of albite

and anorthite, and the transition between both is gradual, the classical concept of isomorphism of the plagioclase feldspars should not be altered in spite of *x*-ray data.

*Note:* A summary covering the above subject was presented at the monthly meeting of the São Paulo Group of the Sociedade Brasileira de Geologia on September 17, 1952, and at the Annual Meeting of the Society at Pôrto Alegre, on November 4, 1952.

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