COORDINATION MODELS

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ABSTRACT

Models of the atomic structures of minerals have been made by considering the structures as assemblages of coordination polyhedra. Tetrahedra and octahedra are the most important coordination polyhedra for mineral structures. Close packed space may be considered as composed of octahedra and tetrahedra, the corners of which may represent the centers of close packed spheres. The polyhedra are in the ratio of two tetrahedra to one octahedron for every close packed sphere. For close packed ionic structures, the centers of mass of anions lie at the corners of the polyhedra, and centers of polyhedra may be occupied by cations or vacant, the proportions of occupied to vacant polyhedra being determined by the chemical formula. In the models, vacant polyhedra are omitted. The method may be extended to non-close packed structures. One size of tetrahedral block and two sizes of octahedral blocks are sufficient to build models of the main framework of nearly all mineral structures. Angles of linkage of polyhedra are regular and evident on inspection.

INTRODUCTION

Models of the type described in this paper have been constructed by Pauling[1] and others. However, as far as the author knows, there is no published account of their construction or indeed any specific account of coordination theory as related to models of the atomic structures of minerals. The models here designated coordination models were constructed in the elementary class in mineralogy at Hamilton College. Because of the simplicity of these models and the ease with which they may be assembled, it is possible to use their construction for a systematic introduction to the atomic structures of minerals. Briefly, structures are conceived as assemblages of regular polyhedra, the corners of which represent the centers of mass of anions, and the centers of which represent coordinated cations. Blocks of appropriate size and shape are used as units of construction. The models represent graphically Pauling's principles[2] governing the structures of ionic crystals. They are concerned with the geometrical and electrical relationships between units of structure. Standard methods of constructing models of the atomic structures of minerals such as the packing models developed at Massachusetts Institute of Technology[3] are, because of the expense and complexity of construction involved, beyond the reach of the elementary student. Moreover, the coordination models specifically point the student towards coordination theory. They reduce the complex geometry of atomic structures to relatively simple patterns involving simple forms.

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[1] Pauling, L., The nature of the chemical bond, Ithaca (**1939**), Figs. 48-2, 6, 9.

[2] Pauling, L., *J.A.C.S.*, **51**, 1010 (1929).

[3] Buerger, M. J., and Butler, R. D., *Am. Mineral.*, **21**, 150–172 (1936).

Modern coordination theory has its origin in the brilliant postulate of the tetrahedral orientation of the four bonds of carbon by van't Hoff and le Bel in the last century. In this century, W. L. Bragg determined structures based on the close packing of oxygen. The fundamental units of ionic structures are visualized as approximately spherical and semi-rigid with characteristic radii and electrical properties. Spheres when packed together so as to occupy the least space (close packed) will enclose amongst themselves, two kinds of openings. If we consider lines joining the centers of close packed spheres, it is evident that within any layer, lines joining the centers of three adjacent spheres enclose an equilateral triangle. If a single sphere of a second layer is placed in contact with the first three adjacent spheres, the lines joining the centers of all four spheres will enclose four equilateral triangles making a regular tetrahedron. Any sphere of radius appropriately smaller than the radius of the close packed spheres might fit in the interstice between the four close packed spheres and would thus be tetrahedrally coordinated. When the array of close packed spheres is extended indefinitely in three dimensions, the ratio of the number of tetrahedral interstices to the number of close packed spheres will be two to one. Still another type of opening exists surrounded by six close packed spheres. The triangles formed by the center to center lines of the six spheres bound a regular octahedron. In extended array, the number of octahedral openings is exactly equal to the number of close packed spheres. Thus, considering the centers of spheres only, close packed space consists of tetrahedra and octahedra in the ratio of two to one. This is a geometrical property of close packed space directly analogous to the hexagonal jointing in columnar basalts.

In inorganic structures, oxygen and less commonly other ions may be found in close packed array. Assuming close packing of oxygen, consideration of the chemical formula for forsterite, Mg_2SiO_4, shows that there is not a sufficient number of cations to fill the available interstices. Therefore the structure will consist of occupied and unoccupied polyhedra. Crystals are built up by a regular repetition of identical groups of atoms or ions and therefore the alternation of these occupied and vacant polyhedra must be systematic and orderly. If Mg atoms are coordinated octahedrally and Si atoms tetrahedrally, only one out of every two octahedral openings and one out of every eight tetrahedral openings will be occupied. Not many arrangements will be found to fit these fundamental requirements. Space group theory imposes no limitations on the number of structures beyond those of symmetry. In a discussion of the 230 space groups, Phillips states, "the *actual* number of different arrangements possible is, of course infinite . . . ."[4] Coordination theory is an

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[4] Phillips, F. C., An introduction to crystallography, London (1946), p. 235.

attempt to reduce this degree of empiricism. Thermodynamic considerations lead Pauling[5] to assume that the octahedral and tetrahedral groupings are a function of the ionic radii; that they persist even when the anions are not in closest packing; and that each ion must be electrically satisfied within a reasonably short distance. Cast in the form of principles governing the structures of ionic crystals, these assumptions are the basis of modern coordination theory.

" . . . we find that very few alternative structures which obey Pauling's law remain open to a mineral of given composition, and one of these alternatives always turns out to be the actual structure of the mineral."[6]

DIADOCHY

Diadochy, or the ability of ions or atoms to substitute for other ions or atoms in a given structural position[7] is subordinated in the coordination models. The models show structural positions and emphasize the structural limitations on diadochy.

GENERAL PROCEDURE

The models so far constructed at Hamilton College are of paper, cut and folded to form individual blocks which are then assembled.[8] Tetrahedra and octahedra, 4 cm. on a side, and octahedra 4.6 cm. on a side are used. When these represent polyhedra of oxygen surrounding cations such as Al''', Si'''', Mg'', and Fe'', the scale is approximately 1.5 cm. equals 1 Angström, or a magnification of 1.5×10^8. A side on the larger octahedra will just bridge the apices of two tetrahedra whose bases join at 120° angles in a common plane. Individual blocks may be painted with colors indicating the nature of the coordinated cation. The blocks are assembled permanently with collodion or any other quick drying cement.[9]

A description of the required structure may be obtained from a number of sources.[10,11] Ordinarily the coordination of the cations will be stated as well as illustrated. Silicon, aluminum, beryllium, boron, zinc, iron, magnesium, and manganese may be tetrahedrally coordinated by oxygen. Aluminum, iron, magnesium, manganese, cobalt, nickel, chromium, titanium, lithium, molybdenum, tungsten, calcium, zinc, and

[5] Pauling, L., *op. cit.*

[6] Bragg, W. L., Atomic structure of minerals, Ithaca (**1937**), p. 36.

[7] Strunz, H., *Zeits. Krist.*, **96,** 7 (1937).

[8] Blocks in hard, colored plastic are being developed.

[9] Several cements with acetone and ether as solvent were tried and found satisfactory. Ordinary mucilage was also satisfactory. The contiguous parts are moistened with cement and held in position while the cement dries. Pins protruding from the vertices were tried and found unnecessary.

[10] Bragg, W. L., *op. cit.*

[11] Wyckoff, Ralph W. G., The structure of crystals, New York (**1931**).

cadmium may be octahedrally coordinated.[12] Large ions such as the alkali metals coordinated by more than six anions are either omitted from the models or are represented by balls mounted on inflexible rods. Small ions coordinated by less than four anions are likewise omitted or are represented by balls. The tetrahedra and octahedra are arranged so as to satisfy the requirements of Pauling's principles. Adjacent polyhedra may share corners, edges, or faces. If polyhedra share a corner, then the charge on the anion represented by the corner is shared equally by the centrally coordinated cations of the polyhedra. If polyhedra share an edge, then two corner anionic positions are common to the centrally coordinated cations. If two polyhedra share a face, then three anionic positions are common to the two centrally coordinated cations. The number of polyhedra common to a single corner anionic position represents the coordination of the anion by cations. This linkage should be clear in the description of the structure. It may be helpful to make a tracing from a diagram showing the positions of atoms, and on the tracing, connect the anions about each cation by straight lines. This should yield a block diagram of the desired model. When the positions of the blocks have been determined, they are glued together. The angular relationships between blocks are in every case simple and evident on inspection. As will be apparent in the description of the models below, use of regular octahedral and tetrahedral blocks leads to idealization of the structures.

When the main principles of the structure are clear, groups of units may be assembled separately and then fitted together. For example, chains of polyhedra are used to construct models of the pyroxenes; double chains of tetrahedra are used to construct models of the amphiboles.

POLYMORPHS OF TiO_2

Figure 1*a* shows a model of anatase, TiO_2, $I4/amd$[13], illustrating the octahedral coordination of Ti'''' with three octahedra meeting at every corner (O). The structure has been idealized by taking as equal, all distances between adjacent oxygens. This is a simplification but not a serious one. In actuality, the oxygen to oxygen distance is reduced slightly if the same pair of oxygens is common to more than one octahedron (an edge is shared), while the distance is increased by the mutual repulsion of the oxygens where the edge is not shared.

Two octahedra are glued together at a corner. A third octahedron is glued between the first two sharing an edge with each. This last octahedron is the central block of the model. A second pair of octahedra shar-

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[12] Bragg, W. L., *op. cit.*, p. 33.

[13] Vegard, L., *Phil. Mag.*, **32**, 65 (1916).

ing a corner is glued beneath the central octahedron in the same manner as the first pair but turned 90 degrees away from the line of the first pair. Since in this structure, all Ti'''' ions occupy equivalent positions, any block may be treated as the central block, and pairs of octahedra disposed above and below it to extend the model. The model in Fig. 1*a* was completed by surmounting the upper and lower pairs of octahedra by square rings of four octahedra. These rings amount to two additional pairs of octahedra each sharing edges with one of the octahedra of the first pairs.

Figure 1*b* is the model of brookite, TiO_2, *Pbca*.[14] Again each Ti'''' ion is octahedrally coordinated by oxygen and each oxygen is common to three Ti'''' ions.

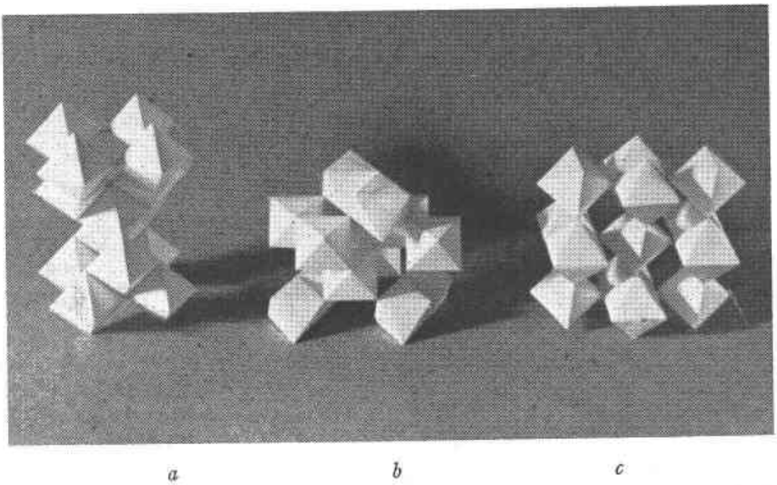

FIG. 1. Polymorphs of TiO_2. (*a*) The unit cell of anatase. The *c* axis is vertical. (*b*) The structure of brookite viewed along the *c* axis with the *a* axis vertical. The unit cell would be complete without the left pair of octahedra on each of the first and third layers from the bottom. (*c*) The structure of rutile viewed along the *c* axis. Lines joining the centers of the paired octahedra enclose the unit cell.

This model also represents an idealized structure. A pair of octahedra are glued together along an edge. Six such pairs are required. Two pairs are aligned on a flat base so that forward faces slope down directly towards the observer. These are the first layer in Fig. 1*b*. A third pair of octahedra is inverted so that forward faces slope up towards the observer. This is the second layer. It bridges the two pairs of the bottom layer. Two pairs make up the third layer. They are oriented like the pair in the second layer with forward faces sloping up towards the observer,

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[14] Pauling, L., and Sturdivant, J. H., *Zeitz. Krist.*, **68**, 239 (1928).

but the alignment of each third layer pair is 60° away from the alignment of the second and first layer pairs. If the model is extended along the *c* axis, all the pairs of octahedra will become parallel zigzag chains.

The fourth layer is begun as a single pair bridging the pairs of the third layer. The octahedra in the fourth layer are oriented like those of the first layer but the pair is aligned parallel to the third layer pairs.

Figure 1*c* is the well known rutile structure, TiO_2, $P4/mnm$[15] viewed along the four fold axis and idealized. Four pairs of octahedra joined together on edges are required. These are joined to a single octahedron in the center as shown in Fig. 1*c*. Four octahedra are then added, one in each corner, each oriented parallel to the central octahedron and each linking two of the four pairs. Note that the corners of each pair of octahedra are connected by the edge of a single octahedron. Note also that the octahedra of the figure may be repeated indefinitely along the line of sight and that each corner octahedron may be considered as a central octahedron in an extended model.

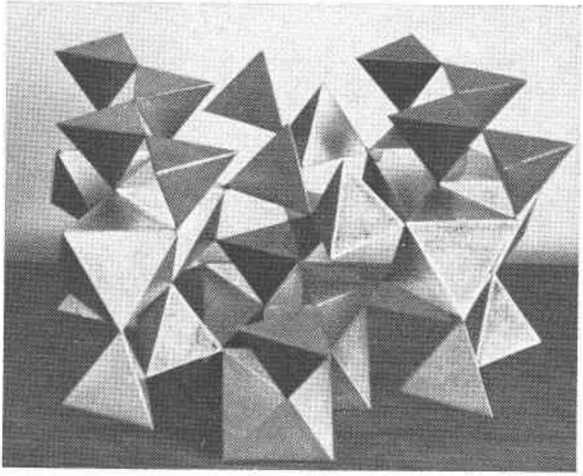

Fig. 2. The structure of diopside. The chains of tetrahedra are parallel to the *c* axis. Note the vertical *c* glide plane perpendicular to the page. The unit cell is only two tetrahedra long in the *c* direction and two thirds of the length illustrated along the *b* axis (from left to right). An additional layer (two chains) of tetrahedra along the *a* axis (linked to the bottom corners of the central octahedral chain) would complete the unit cell in that direction.

DIOPSIDE

Figure 2 is a reproduction of a photograph of a model of a portion of

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[15] Vegard, L., *op. cit.*

the unit cell of diopside, $CaMgSi_2O_6$, $C2/c$,[16] showing the linkage between chains of silica tetrahedra and magnesia octahedra. Calcium atoms (not shown) occupy the irregular octahedral embayments between the magnesia chains and the apices of the silica tetrahedra.

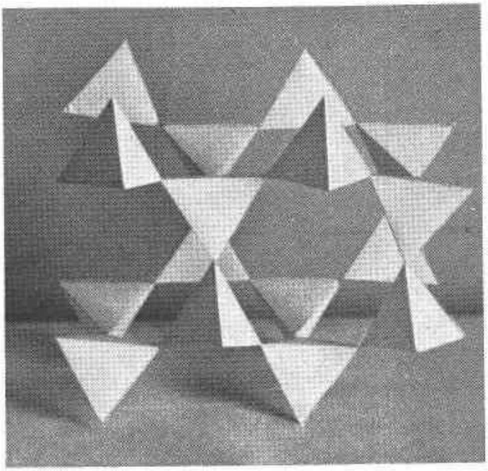

FIG. 3. The structure of tridymite viewed along the *c* axis. The eight tetrahedra in front were assembled as a unit. The eight tetrahedra behind are a reflection of the first unit, joined to it along apices. The unit cell would be complete without the four tetrahedra on the left side of the model.

TRIDYMITE

Figure 3 is a model of tridymite, SiO_2, $C\bar{6}2c$ or $C6/mmc$,[17] built by Joseph Hull. This illustrates the extended linkage of the SiO_2 minerals. The tetrahedra are assembled point to point in hexagonal rings with apices pointing alternately up and down. One ring is fitted on top of another, apex to apex. By extension in three dimensions, the network structure is developed. There are two ways of fitting the rings together apex to apex, the one illustrated by the model and an alternate. The alternate assembly is the structure of cristobalite, SiO_2, $Fd3m$(?). Higher symmetry should be characteristic of higher temperature, and cristobalite is the high temperature form of SiO_2 next above tridymite.

Our experience at Hamilton College has been that these models greatly simplify the study of mineral structures. We have found the assembly of these models to be well within the abilities of beginning students in mineralogy.

Manuscript received July 21, 1951

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[16] Warren, B. E., and Bragg, W. L., *Zeits. Krist.*, **69**, 168 (1928).

[17] Gibbs, R. E., *Proc. Roy. Soc.*, **A113**, 351 (1927)