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## ISOMORPHOUS SUBSTITUTION OF ELEMENTS IN MINERALS\*

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The fact that certain elements could substitute for others in chemical compounds was known for some time before the concept was introduced into mineralogy and chemistry. Mitscherlich, during his chemical work on the salts of arsenic and phosphoric acids in 1819, noted that crystals of corresponding salts of these acids resembled each other very closely in habit and angles and, not having at that time the means of accurate measurement, he believed that they were identical. In 1821 he introduced the term "isomorphism" in mineralogy, with the following explanation: "An equal number of atoms similarly combined produce the same crystal form, independent of the nature of the atoms but determined by their relative position."

Previous to this, in 1811, Haüy announced that each chemically pure substance, when crystalline, possessed its own characteristic angle, which has since been proven one of the fundamental laws of crystallography. This was opposed to the conception of Mitscherlich, as in his opinion isomorphous substances possessed identical angles.

The controversy following these opposing views was not settled for years, but was materially allayed by Wollaston who, having invented the reflecting goniometer in 1812, announced that the orthorhombic sulphates and carbonates of barium, strontium and lead showed consistent measurable differences, though these differences were small. The enormous mass of data accumulating since reaches much farther, and adds that the angles in isomorphous groups are a function of the chemical composition.

Thus the law of isomorphism was narrowly restricted to those

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chemical compounds with like number of atoms and configuration; but, restricted as it was, it served, in the hands of chemists, as a reliable means of deciding in some cases between combining weight and atomic weight. It was also rated by Mendeléeff as one of four exact guides or indices used by him in the construction of the table of the elements which bears his name and has stood the test of time for the last sixty years.

At the close of the nineteenth century, all the possible types of symmetry and homogeneous point-systems, after which crystals could be constructed, were mathematically determined. However, those individuals with the most active imagination did not believe it would ever become possible to measure the distance between the atoms in these point-systems; but with the advent of Laue's photographs, the determination of the length of the  $x$ -ray wave, the modifications of the Braggs, and the interest of many other workers, the point-systems have been proven to be in reality facts and not theory. We are able at the present time to put our finger on any atom in the crystal structure of a chemical compound; possibly not with complete exactness in the case of complex molecules, but certainly with full confidence in the case of the more simple. This knowledge has changed in several ways our conception of crystal structure. Mendeléeff considered the molecular volume, the result of dividing the molecular weight by density, or a multiple, as the unit of structure, or the brick used in the crystal building.

When the space relations of the atoms in halite, a simple chemical compound, are considered, where these relations are known with exactness, molecular boundaries at once fade away. Each chlorine atom is equidistant from six sodium atoms, and each sodium atom is equidistant from six chlorine atoms. There is no unique atom among the six with which to tie a chlorine atom representing the chemical formula,  $\text{NaCl}$ , although atoms are found in the crystal in the correct proportions as represented by the chemical formula. This is true of most mineral crystals and valence relations, as known in many organic compounds, liquids and gases, are lost. The ionic forces still remain, but apparently with quite a different distribution, as in sodium chloride the single valence of chlorine has no choice between six sodium ions, but from point of view of distance must necessarily be equally attracted by each.

For convenience in description and comparison, an imaginary

crystalline unit has developed, which was defined by the Braggs in the following manner: "The unit of cell structure is the smallest portion of a crystal which, repeated through space without change in character or orientation, makes up the crystal." All atoms and bonds in the proportions required by the chemical formula will be contained in the unit, as well as all physical properties and symmetry of the crystal will be represented. The crystal is constructed by simply placing one unit beside another, as the bricks in a wall. It is within this unit of structure that isomorphous elements are substituted, and the resulting modifications of volume, angles and all other physical properties are the resultant or summation of forces interacting within the unit. These forces are both attractive and repulsive, polar and non-polar; and the internal space arrangement of atoms in the unit is the resultant or equilibrium attained by these interactions and may be modified by temperature and pressure. The attraction between atoms, which has become known as Van der Waal's cohesive force, and the electrostatic forces due to valence ionization, are the determinative forces in the growth of a crystal, and of these Leonard-Jones and Dent<sup>1</sup> say that "the Van der Waal field falls off according to a second or third power of the distance and so becomes of greater importance than the electrostatic at a long distance" and suggests that Van der Waal's forces act as the first agent in the process of capturing atoms at the surface of growing crystals, and the electrostatic force clinches the capture and fixes the atom in the crystal and presumably the relation in the crystal unit. The distance between pairs of atoms of any two elements, as measured in crystals, varies with the compounds, the pressure with which they are forced together depending upon their chemical affinity and valence. Gibbs believed that this distance varied with the binding forces and was inversely proportionate to the valence. The combining radius of an atom varies when measured in compounds of quite different chemical character; and whether the atoms or ions fill space or not, their relative positions represent equilibrium, or the resultant of attractive and repulsive forces interacting between them. In sodium chloride, where the valence of chlorine is one and sodium also one, each chlorine atom is equidistant from six sodium atoms in the direction of the cubic faces, and the field of influence or domain is usually considered as a sphere with six flattened facets parallel to the cube, or six areas

<sup>1</sup> Leonard-Jones and Dent, *Trans. Faraday Soc.*, vol. 24, p. 92, 1928.

in common to the sodium and chlorine atom. Whether this represents the atom of an element or its reaction limits is immaterial. The pressure areas will increase in size with the increase of pressure.

In the case of an individual atom, surrounded by neighbors in the network exerting various pressures, the original sphere will be distorted and the resultant lines of force will vary and thus become directional, a characteristic of the physical property of crystals. The atom reacting under the varied pressures as a loosely inflated ball, its radius of combination changes in direction with pressure, both shape and volume depending on the co-ordinate number of its positions within the crystal unit. Bragg<sup>2</sup> notes that the interatomic distance between oxygen atoms in the silicate may vary from 2.5 to 2.9 Å according to their position, leading to a considerable variation in volume. If this be true, then atoms of the same elements in a crystal are not by any means surrounded by the identical conditions in regard to space and interacting forces. In one position the atom may be replaced with ease, while in another with great difficulty, if at all. In forsterite  $Mg_2SiO_4$ , of the olivine group, there are two positions of magnesium atoms, an equal number of each. One set lies at a center of symmetry, sharing a pair of oxygen atoms with two tetrahedra; and the other set, with only one tetrahedron.<sup>3</sup> In the crystal structure of monticellite<sup>4</sup>  $(MgCa)SiO_4$ , the isomorphous calcium atom has been substituted for one set of magnesium atoms, without changes in symmetry but with increase of cell dimensions due to the greater atomic diameter of calcium. It would be interesting to know which set of magnesium atoms have been displaced; whether it is the same set in which ferrous iron is substituted to form olivine or whether, due to the smaller size of the iron, it is the other set which is displaced; indicating that the two sets of magnesium atoms are quite different in their isomorphous tendencies.

In this same unit structure of  $Mg_2SiO_4$ , (4 to the unit,) there are three positions of oxygen atoms, which would also possibly represent three degrees of isomorphism, if there were any elements capable of being substituted for oxygen in this structure. Warren<sup>5</sup> in his work on the crystal structure of tremolite points out that

<sup>2</sup> Bragg, W. L., *Zeit. Krist.*, vol. 74, 278, 1930.

<sup>3</sup> Bragg, W. L., *Zeit. Krist.*, vol. 74, 241, 1930.

<sup>4</sup> Brown, G., and West, J., *Zeit. Krist.*, vol. 66, 154, 1927.

<sup>5</sup> Warren, B. E., *Zeit. Krist.*, vol. 72, 42 and 493, 1930.

the chemical formula should be  $H_2Ca_2Mg_5(SiO_3)_8$ , with two molecules in the crystalline unit. Eight magnesium atoms are similarly located in the crystalline lattice; but two atoms, or one in each chemical molecule, hold an unique position. Berman and Larsen<sup>6</sup>, in their study of a hundred analyses of alkali amphiboles, have reported that in the substitution of isomorphous atoms for magnesium there is always one of the five magnesium atoms remaining and not displaced. It is natural to conclude that this is the unique atom, and that it is able to hold its position against all applicants is due to the ionic attractions surrounding it, or to its co-ordinate position. They also point out other limited substitutions; as aluminum never substitutes for more than two atoms of silicon. A possible explanation of this is that an atom of aluminum coupled with an atom of sodium replaces a silicon atom, the sodium occupying the vacant place in Warren's lattice of the amphiboles.

#### RADII OR VOLUME OF ATOMS

Undoubtedly atoms of equal volume or radii, or more particularly of equal domain, have a great tendency to substitute for each other, and especially so when the isomorphous minerals contain the same number of atoms and the same configuration in the lattice. If the volume were exactly equal, this would amount to the same as taking a brick out of a wall and slipping in another of the same size but of different material and color. But all atoms are not of the same volume, as is shown by Wherry's<sup>7</sup> table of atomic volumes. Following the principles expressed by Wherry<sup>8</sup>, we would expect sodium and magnesium, differing in radii by  $.05\text{\AA}$ , to substitute for each other under most varied conditions; but the experience is that calcium and sodium change places more often, differing in radii by  $.25\text{\AA}$ .

If the historically noted isomorphous group of rhombohedral carbonates is considered, calcium, with an atomic radius of  $1.75\text{\AA}$  and a volume of 22.4, differs considerably from iron with a radius of  $1.30\text{\AA}$  and volume 9.2, and from manganese, lying next to calcium, with a radius of  $1.50\text{\AA}$  and a volume of 14.9; nearly three times the volume in one case and double in the other. There must certainly be other compensatory factors or variables to allow this substitu-

<sup>6</sup> Berman, Harry, and Larsen, E. S., *Am. Mineral.*, vol. 16, 140, 1931.

<sup>7</sup> Wherry, E. T., *Am. Mineral.*, vol. 9, 165, 1924.

<sup>8</sup> Wherry, E. T., *Am. Mineral.*, vol. 8, 1, 1923.

tion and not at the same time change the symmetry of the type. The lattice of the calcite atoms is the face centered rhombohedron in which the three oxygen atoms<sup>9</sup> are not definitely fixed, but are symmetrically arranged around the trigonal axis and may be moved back and forth along this axis, or farther away from it in the basal plane, without affecting the symmetry, thus introducing a compensation for the variable volume of entering isomorphous atoms.<sup>10</sup> The sulphur atoms in pyrites are also movable on the trigonal axis in a like manner. Other examples have been noted, enough in fact to form an important group when considered from the isomorphous point of view.

In the space-lattice of crystals where all units of structure are identical, or in other words where no isomorphous atoms have been substituted, the structure is supposed to be at equilibrium and without strain. In the substitution of isomorphous atoms a strain is immediately set up in the structure which increases with the percentage of substitution. In the isometric system this strain is indicated by a linear change of the cubic edge. In types of lower symmetry, it is indicated by variation of angular change as well. Linear changes in the substitution of manganese for calcium in the above carbonate series represents an ideal pair where complete substitution may take place from either end without change in symmetry. In the same substitution, where the larger atom of calcite has taken the place of a smaller atom of manganese, there is a continuous increase of the space between the rhombohedral planes, from 2.85 Å<sup>11</sup> in rhodochrosite to 3.075 Å in calcite, and an increase of the rhombohedral angle of from 73° to 74° 55'. At the same time the oxygen atoms have moved farther away from the center of the larger calcium atom as well as from the carbon atom.

In the substitution of calcium for magnesium and vice versa, the strains become so great that when the proportion of 1:1 is reached a change of symmetry takes place and a new phase, dolomite appears. Also, as reported by Pabst<sup>12</sup>, in the case of gold crystallizing in the isometric close-pact atoms with an atomic radius of 1.45 Å, and mercury crystallizing in the hexagonal nearly close-pact atoms with an atomic radius of 1.60 Å, the mercury enters the gold

<sup>9</sup> *Phil. Mag.*, ser. 6, vol. 40, 169, 1920.

<sup>10</sup> Wyckoff, R. G. W., *Am. Jour. Sci.*, 4th Series, vol. 50, 317, 1920.

<sup>11</sup> Krieger, Philip, *Am. Mineral.*, vol. 15, 23, 1930.

<sup>12</sup> Pabst, Adolf, *Z. Physik., Chem.*, abt. B, vol. 3, 443, 1929.

lattice up to 15 per cent, but somewhere between that and 20 per cent the symmetry changes to the hexagonal symmetry of mercury. Aluminum and zinc are a similar pair. Zinc, with an atomic radius of  $1.40\text{\AA}$  and a hexagonal symmetry, enters the aluminum (atomic radius  $1.35\text{\AA}$  but with an isometric symmetry) lattice to the amount of 15 atomic per cent.<sup>13</sup> The rigidity of the aluminum lattice resists further stress and substitution ceases leading to limited isomorphism, though the radii are very close in size but differ in directional forces; while two metals, silver and gold, with the same difference of atomic radii  $.05\text{\AA}$  but with like symmetry, substitute for each other from end to end. Copper and nickel, both isometric but with a difference of  $.25$ , form a complete series.

The compressibility of solid elements and its bearing on isomorphism has been emphasized by Richards<sup>14</sup> and illustrated by a curve which follows very closely the atomic volume curve of Lochar Meyer, indicating very strikingly that the elements having large atomic volume are more highly compressible; since the forces surrounding an atom in a crystal may be considered as pressures of considerable magnitude their results will be quite different on atoms differing in volume.

This variable compressibility of the elements must be considered as a factor in isomorphism which enables the atom to adjust itself, not only to the space to be occupied in a given lattice, but also to the irregularities of such space. These irregularities will depend upon the co-ordinate number of the position. The greatest encroachment on, or flattening of, the atomic domain of the substitute will be in the direction of the greatest force; and with pressures from all sides it would, therefore, seem that large interatomic spaces cannot exist in the crystalline lattice not dominated by the surrounding atoms; and in cases where an element is found by analysis to be present in excess of the proportion required by the chemical formula, it probably exists by reason of discontinuities of the crystalline lattice, and therefore must be of the nature of inclusions, often submicroscopic, as a product of exsolution.

#### TEMPERATURE

Temperature is still another controlling agent in the substitution of atoms in the crystalline lattice. In the rise of temperature

<sup>13</sup> Rosenhein, Walter, *Trans. A.I.M. & M.E.*, vol. 59, 1.

<sup>14</sup> Richards, T. W., *Trans. Faraday Soc.*, vol. 24, 111, 1928.

the binding forces are gradually overcome until the structure either changes in symmetry, by unequal expansion or contraction, and a new crystalline phase occurs; as in the case of leucite, and  $\beta$  phases of various minerals as quartz; the orthorhombic  $\text{Ag}_2\text{S}$ , acanthite, becomes isometric argentite above  $180^\circ$  or it breaks down entirely at the fusing point.

It would be perfectly natural to expect two elements, as aluminum and ferric iron, with atoms of almost the same volume, with chemical properties so nearly alike that it is almost impossible to separate them quantitatively, same valence, crystallizing with the same symmetry both as elements and as oxides, to be isomorphic in their simple compounds; and it has been generally urged in the past that atoms, not isomorphous to any great extent in simple compounds, may become so in more complex compounds, by reason of the greater chances of readjusting the interacting forces. We would expect, therefore, to find in nature a feldspar in which ferric iron has substituted for aluminum to a considerable extent, but this substitution is exceedingly rare. However, D. Beliankin<sup>15</sup> has reported an orthoclase from Madagascar with considerable ferric iron in the crystalline lattice; but usually the pink or red orthoclases are colored by inclusions of hematite, the ferric oxide entering the lattice at high temperatures, due to the weakening of the crystalline forces, and even then only to the amount of 2 or 3 per cent, becoming metastable on cooling, with the iron finally forced out as inclusions.

Probably the best example of isomorphism at higher temperatures is that of orthoclase ( $\text{KAlSi}_3\text{O}_8$ ) and albite ( $\text{NaAlSi}_3\text{O}_8$ ), which form a single homogeneous lattice, probably in all proportions at  $1050^\circ\text{C}$ , separating in the well known perthites on cooling, where each component is a limited isomorphous crystal of the two silicates. The structure of perthite may be so fine and intimately mixed as not to be recognizable with the microscope, or submicroscopic. In such cases the complex nature becoming apparent only after application of  $x$ -ray methods, Kozi and Endo<sup>16</sup> found that in moonstones from Ceylon and Korea, the Laue spots were peculiarly double at ordinary temperature, which they interpreted as indicating two lattices, one representing orthoclase and the other albite. Upon heating these specimens at  $500^\circ$ , one set of spots began to ap-

<sup>15</sup> Beliankin, D., *Bull. Ac. Sci., U.S.S.R.*, 571, 1929.

<sup>16</sup> Kozi and Endo, *Sci. Rep. Tohoku Univ., Sendai*, 3d ser., vol. 1, 1, 1921-1923.



proach the other; and at 1060° only one set remained, and the specimen represented one homogeneous lattice. On cooling, the lattices separated and, at 700°, again reverted to their original position with double spots.

Perthitic structures occur in groups of minerals other than feldspars. If the same interpretation is applied, they represent isomorphism at higher temperatures and separate as mixtures at lower temperatures.

#### CONCLUSION

Undoubtedly volume is a prime factor in isomorphism, but I have attempted to show that there are other factors of equal importance even where the atoms are practically of the same size, such as (1) the coordinate position of the atom in the crystalline lattice; (2) atomic directional forces probably due to pressure; (3) the variable compressibility of the atoms; (4) differential expansion of the atoms with a rise of temperature; and lastly (5) the weakening of the crystalline forces with a rise of temperature. Many additional illustrations could have been noted justifying the assumed complex nature of isomorphism which, however, would only tend to exhaust your patience and add but little strength to the thesis.