VOLUME ISOMORPHISM IN THE SILICATES[1]

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The recent demonstration, by the application of X-rays to the study of crystal structure, that the dimensions of atoms remain fairly constant and definite from one crystalline compound to another appears to necessitate a revision of the current views of isomorphism. To make this evident it is only necessary to list the volumes which atoms of some of the elements have been found by various workers (especially W. L. Bragg) to occupy, and, assuming crystals to be essentially close-packed structures, to consider the consequences of the relations brought out. The results of X-ray measurements are usually reported in terms of atomic diameters, but they may be transformed into volumes by using the approximate formula: $V = 4.2 \ (d/2)^3$, the unit becoming 10^{-24} cc. The elements vary in volume more or less—perhaps $\pm 30\%$ of the mean value—from one mode of combination to another. The mean values which seem most likely to be represented in the silicates, estimated from the data available, are given here in increasing order:

ELEMENT	VOLUME	EL.	VOL.	EL.	VOL.
O	1	Cr	10	Ca	22
F	$1\frac{1}{2}$	Fe	10	Na	23
C	2	Al	11	Sr	31
H	5	Ti	12	Ba	38
Cl	5	Mg	13	K	38
Be	7	Mn	14	Rb	47
Si	7	Li	15	Cs	55

[1] Read at the meeting of the Mineralogical Society of America, Ann Arbor, Michigan, Dec. 29, 1922. At this meeting Dr. H. S. Washington called attention to the fact that Professor F. Zambonini is working along similar lines. However, as his writings on the subject are not accessible to the writer, and as considerable interest was shown in the data, it has been decided to publish the paper as presented, with the understanding that in case it shall turn out that Professor Zambonini has already reached the same conclusions as to certain of the minerals, his claims to priority will not be questioned. Independent arrival at a given viewpoint enhances the probability of its essential correctness.

REQUISITES OF ISOMORPHISM.—It has long been held that in order to be able to replace one another, elements must be chemically analogous and of equal valence. The latter can only be regarded as applying, however, to elements while in the liquid or gaseous states; for there is good reason to believe that on entering the crystalline form, the valence of an atom may change completely. Sodium nitrate and calcium carbonate are isomorphous, even tho the valences of the constituents other than oxygen are, in the liquid state, dissimilar, for X-ray study shows that in the solid state sodium becomes homologous with calcium, and nitrogen with carbon. This and similar cases are best looked upon as representing what may be termed "double isomorphism" and symbolized in some such manner as: $[(Na,Ca)+(N,C)]$.

It now seems more probable that the principal requisite of isomorphous replaceability is that the elements in question must possess approximately identical volumes, at least in simple compounds, the crystal structures of which represent fairly close packing of the constituent atoms. The principle of mass-isomorphism, the validity of which is emphasized by the present viewpoint, indicates, however, that the more complex the compound the more chances there are for readjustments to occur, and the greater the differences in volume of the mutually replacing atoms may be.

In this article it is proposed to discuss the application of this viewpoint to the interpretation of the compositions of certain silicates. Before taking up special groups of these it may be pointed out that the lack of isomorphism between carbonates and silicates, in spite of their presumably similar valence relations, has often been commented upon. The volume data furnish an adequate explanation, however, for carbon occupies less than one third as much space as silicon, and a structure which would be stable when including the one would be almost certain to become unstable should the other tend to enter.

THE FELDSPAR GROUP.—The chief peculiarites of the isomorphism in this group are (1) the limited replaceability of sodium and potassium, (2) the complete isomorphism of albite and anorthite, and (3) the isomorphism of the potassium mineral orthoclase with a barium compound in hyalophane or "baryta-

orthoclase." That these relations actually involve the molecules has been demonstrated by the X-ray studies of Hadding.[2]

An adequate reason for (1) is to be found in the decidedly dissimilar volumes occupied by the sodium and potassium atoms. Feature (2) has been fully discussed in a recent paper.[3] The volumes of sodium and calcium are essentially identical, while the volume of aluminium is but slightly greater than that of silicon, so that double replacement $[(Ca,Na)+(Al,Si)]$ as required by the valence relations in solution, takes place. It is interesting to note that (3), the replaceability of potassium and barium is likewise based on their equality of volume. Analyses of barium-bearing feldspars show more or less parallel increase of silica and potash contents, indicating that here as in the plagioclases simultaneous replacement of aluminium and silicon occurs. The formulas of the end members of this series are, accordingly, $K(AlSi_3O_8)$ and $Ba(AlAlSi_2O_8)$ and the replacement is not "(Ba, K_2)" as often stated, but $[(Ba,K)+(Al,Si)]$.

LEUCITE GROUP.—The mineral analcite, usually formulated $Na(AlSi_2O_6).H_2O$ or $Na_2Al_2(SiO_3)_4.2H_2O.XH_2Si_2O_5$, is often included among the zeolites; in the opinion of the writer this is incorrect (as recognized in Doelter's Handbuch der Mineral Chemie) for a number of reasons, including the following: It occurs as a primary constituent of igneous rocks; it contains little water, and loses this before the blowpipe without the bubbling which the term "zeolite" implies; and it does not show the peculiar dehydration phenomena characteristic of most true zeolites, such as loss of H_2O below 100° C and in several definite stages. Moreover it exhibits features and anomalies of crystallization which correspond closely to those of leucite, $K(AlSi_2O_6)$, and the one mineral can be transposed into the other at will by mere treatment with the hydroxide of the alternate alkali metal. The two minerals are accordingly regarded as belonging to one and the same group.

The striking fact that the potassium salt is anhydrous while the sodium salt contains water of crystallization is capable of adequate explanation on the basis of the volume relations. If the atoms in the crystals of leucite are closely packed, then when the smaller sodium atoms enter the same structure, gaps are left, and

[2] *Lunds Univ. Årsskrift*, N. F., [2], **17**, No. 6, 26 pp., 1921.

[3] *Am. Min.*, **7**, 113, 1922.

a simple way for these gaps to be occupied is by water, which is present while the mineral is crystallizing. This seems unable to fill the gaps completely, however, and as shown by Foote and Bradley,[4] in some cases hydrous albite or more probably silica enters. In others a hypothetical hydrous carnegieite (Parsons[5]) or perhaps mere natrolite is taken up. In such cases the solid solution is non-isomorphous and the agreement between the structures of the main compound and the dissolving ones need not be close. The replacement, then, is not merely (K, Na) but [K, $(Na+H_2O+X)$]. The formula of analcite may accordingly be written $(Na+H_2O+X)$ $(AlSi_2O_6)$.

PYROXENE GROUP.—Of the many cases of isomorphism in this group, the following may be selected for discussion: (1) The practically complete replaceability of Mg and Fe,'' but slight tendency of Ca to replace either; (2) the existence of lithium and sodium, but the lack of potassium pyroxenes; and (3) the improbability of the Tschermak molecule, R'' R'''_2SiO_6.

As to (1), it is easy to see a reason for the relations existing, for the volume of magnesium is closer to that of iron than to that of calcium. The lithium and sodium pyroxenes (2) are likewise readily accounted for. Starting from diopside, $CaMg$ (Si_2O_6), the calcium atom is identical in volume with sodium, but the valence relations in the solutions require that this replacement be accompanied by the simultaneous entry of a trivalent atom. Both iron and aluminium approach magnesium in volume, so the exchange is easily consummated: the isomorphous replacement is [(Ca,Na)+(Mg,Al)] or [(Mg,Fe)], giving jadeite and acmite respectively. Lithium is distinctly smaller than sodium, and so, as in the case of entry of a small atom in place of a large one discussed under the preceding caption, gaps result from its occupation of the pyroxene structure. This time, however, the gaps are not filled by the entrance of water at the start, probably because they are too small. Instead, their presence makes itself manifest by the marked alterability of the resulting mineral, spodumene. The space required by the potassium atom, on the other hand, is evidently too great to permit this element to enter the pyroxene structure at all. (3) The Tschermak hypothetical molecule (Mg, Fe'') (Al, Fe''')$_2$(SiO$_6$) would be entirely possible

[4] Am. J. Sci., 33, 433, 1912.
[5] Univ. Toronto Studies, Geol. Series, No. 14, p. 32, 1922.

from the valence viewpoint; but now that isomorphism is proving to be more a matter of volume than valence, the probability of its real existence requires attention. Starting from the formula of diopside-hedenbergite, $(Mg,Fe) Ca(Si_2O_6)$, the Tschermak molecule would represent the result of simultaneous replacement of (Ca,Al) (or Ca,Fe''') and (Si,Al). The first change corresponds to so marked a decrease in volume that the existence of the Tschermak molecule seems at least improbable. The excess alumina might, however, represent $AlAlO_3$ replacing $MgSiO_3$, and fit the volume relations better.

AMPHIBOLE GROUP.—All that has been said concerning the pyroxenes applies with essentially equal force to the amphiboles. The amphibole structure appears to be less closely packed than the pyroxene, however, as the specific gravity is lower and a distinct amount of water is often taken up in solid solution, which presumably implies the filling of structural gaps.

BERYL GROUP.—The alkalies present in some occurrences of beryl are usually considered to represent the replacements (Be, Cs_2), (Be, Li_2), etc. The volume relations show rather definitely that these replacements cannot take place. The atoms of even the smallest alkali metal, lithium, are twice and of cesium many times as large as the beryllium atom. Inspection of the analyses shows, moreover, that the silica content decreases markedly as the alkali content rises, indicating that the presence of alkalies in beryl is connected with the entrance of a compound with different ratios, in some form of solid solution. This compound is not known among minerals, although plotting the SiO_2 against the alkali content shows it to be related to pollucite, and to have a composition approximating $H_2O.Li_2O.Cs_2O.2Al_2O_3.9SiO_2$.

NEPHELITE GROUP.—The potassium and sodium members of this group form an interesting analogy with those of the leucite group already considered, although the ultimate result is somewhat different. Admitting that the structure is reasonably closely packed when potassium is present, in kaliophilite, $K(AlSiO_4)$, the entrance of the less voluminous sodium to form nephelite, $Na(AlSiO_4)+X$, leaves gaps. Here instead of water + silica, only excess silica is taken up. This silica has been suggested[6] to be present as (Si_3O_8) groups replacing (SiO_4) groups, but as shown in the paper on the plagioclases already cited, volume

[6] By Clarke, Schaller and others.

relations in general do not fit in with such a replacement, and another interpretation seems called for. The excess silica may as well be considered "silica-of-crystallization," for the volumes indicate the formula of nephelite to be $(Na + XSiO_2)$ $(AlSiO_4)$.

GARNET GROUP.—Isomorphism in the garnet group proper comprises the replacements (Mg, Ca, Mn, Fe'') and (Al, Cr, Fe'''). The volumes of the trivalent metals here represented are all essentially identical. Among the bivalent ones, calcium is larger, and iron smaller, than the other two, but the differences are not great enough to prevent fairly complete mutual replacement. This group accordingly represents one of the best marked instances of isomorphism among minerals. Such gaps as exist, as that between pyrope and spessartite, appear to be of chemical rather than volume origin. Titanium, judging from its volume, should be able to replace the trivalent elements, but probably not more than in very slight degree the decidedly smaller silicon. The constitution of schorlomite therefore seems to require study by modern methods, before the formula assigned to it can be accepted in full. The fact that in the chrysolite group calcium is less isomorphous with other bivalent elements than they are among themselves accords with the volume relations.

SCAPOLITE GROUP.—The rather complex isomorphism represented in the scapolites corresponds to the volume relations in a striking way. The two end-members are meionite, $Ca_4(Al_6Si_6O_{25})$, and marialite, $Na_4(Al_3Si_9O_{24}Cl)$, or sulfate or carbonate equivalents of the latter. The replacement of the four calciums of the first by four sodiums involves no volume change; the simultaneous replacement of three aluminiums by the slightly smaller silicons may leave some gaps in the structure, and the loss of one oxygen necessitated by the valence relations increases these. It is therefore to be expected that other elements or groups could find a place, and the entrance of chlorine, (HSO_4) and (HCO_3) is a natural consequence. If it were only possible to ascertain which of the analyses of vesuvianite recorded in the literature were not made on mixtures, its constitution could no doubt also be satisfactorily interpreted on the volume basis.

TOURMALINE GROUP.—The various replacements of atoms with one degree of valence by those with another which occur in this group, such as (Fe'', Li) and (Al, Mg), correspond well with the volume relations. It is especially noteworthy that in spite of the

mass effect connected with the large size of the molecule, calcium seems unable to enter.

ZEOLITE GROUP.—Several of the minerals in this group have been regarded as illustrations of the replacements (Ca, Na_2) and (SiO_4, Si_3O_8), which replacements, as pointed out in the paper on the plagioclases above cited, are from the volume viewpoint improbable even though the packing of the atoms in the zeolites is not very close, as the dehydration phenomena suggest to be the case. However, the analyses are open to other interpretations. In some zeolites there is a fairly good indication that the Ca and Na are present in definite proportions, as pointed out in Dana's System. That this is true of thomsonite can readily be seen if the silica content is plotted against the soda, as has been done in a paper presented in connection with this one.[7] Allowing for a certain number of analyses having been made on mixtures, it seems true also of mesolite, stilbite, phillipsite (K instead of Na), etc.

The variable composition of chabazite has even been interpreted as due to two replacements, (SiO_4, Si_3O_8) and (Ca, Na_2), independently of one another. There is, however, no proof that the solid solution in chabazite is really of isomorphous type, and there may well be non-isomorphous solid solution of one or more of the associated zeolites.

MICA GROUP.—Analyses of some muscovites show a considerable excess of silica over that required by the normal formula, and a special varietal name, phengite, is applied to them. This has been interpreted as indicating the replaceability of SiO_4 and Si_3O_8, but when the three variable constituents of the phengites in Dana's System, SiO_2, Al_2O_3, and $(Mg, Fe)O$, are plotted in a triangular diagram, they range, not toward a mere "trisilicate," but toward a molecule with the composition $H_4K_2 (Mg,Fe)(Al_4Si_7O_{24})$. Comparing this with the normal muscovite formula $H_4K_2(Al_6Si_6O_{24})$, it can be seen to represent the double isomorphous replacement $[(Al, Mg)+(Al, Si)]$, the volume relations being adequately satisfied. The variability in composition of other micas, chlorites, etc., is in many if not all cases capable of interpretation in similar ways.

SUMMARY.—By applying to certain silicates the view that isomorphism is connected with volume rather than valence rela-

[7] To be published in a subsequent number.

tions, it is possible to explain many of their peculiarities of composition in a simple manner as follows: In the feldspar group, the fact that the replaceability of potassium for sodium is limited, but for barium is more complete, the relation being one of double isomorphism, $[(Ba, K)+(Al, Si)]$; in the leucite group, the significance of the water in analcite, which is not a zeolite, the formula being $(Na+XH_2O+X)$ $(AlSi_2O_6)$; in the pyroxene group, the lack of potassium members, and the improbability of the existence of the Tschermak molecule; in the beryl group, the presence of alkalies as due to solid solution of a pollucite-like substance; in the nephelite group, the probability that the excess silica is silica-of-crystallization, $(Na+XSiO_2)$ $(AlSiO_4)$; in the garnet group, the extensive isomorphism; in the scapolite group, the homology of meionite and marialite, and the reason that sulfate and carbonate groups can enter; in the tourmaline group, the possibility of replacement of Li for Fe'' and Al for Mg; in the zeolite group, non-existence of (Ca,Na_2) and (SiO_4,Si_3O_8) replacements, and the explanation of variability as due to admixture or to non-isomorphism; and finally in the mica group the absence of evidence of (SiO_4,Si_3O_8) replacement, phengite approaching for instance H_4K_2 (Mg, Fe) $(Al_4Si_7O_{24})$, which represents double isomorphism $[(Al, Mg)+(Al, Si)]$.

NOTE ON LEUCHTENBERGITE FROM PHILIPSBURG, MONTANA[1]

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A white chlorite occurring in metamorphosed limestones of the Philipsburg district of Montana was mentioned by Calkins[2] under the name leuchtenbergite. Several other white chlorites having been described since the publication of this paper, Mr. Calkins requested that his specimens, which were preserved in the National Museum, be reëxamined. The chlorite has been analyzed in the museum laboratory, and the results of the analysis confirm the original identification, the mineral being a typical leuchtenbergite. The specimens examined are numbered P 480 in the type collection from the Philipsburg district. Since the

[1] Published by permission of the Secretary of the Smithsonian Institution.

[2] Calkins, F. C., Geology and ore-deposits of the Philipsburg Quadrangle, Montana. *U. S. Geol. Survey, Prof. Paper* 78, 161, 1913.