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THE PLAGIOCLASE FELDSPARS AS A CASE OF ATOMIC ISOMORPHISM

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The peculiar composition of the plagioclase feldspars was first rationally explained by Tschermak,[1] and his view that they represent solid solutions of two end-members, albite and anorthite, has gained general acceptance. The crystallographic, physical, and fusion phenomena show that the solid solution is of isomorphous character.

The empirical formulas of the plagioclase end-members are $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ respectively. Because these two formulas are of apparently dissimilar chemical type, there have been numerous attempts to account for this instance of isomorphism. These fall more or less definitely into three groups: (1) The structural formula viewpoint, which assumes that the elements retain the same valence in the solid that they have in the liquid form, and that isomorphism of metals is always valence for valence, but that widely dissimilar acid radicles may be isomorphous; (2) the arithmetical viewpoint, which finds in simple integral relationships between constituents or their properties sufficient explanation for isomorphism; and (3) the atomic isomorphism viewpoint, which admits isomorphism only between mutually similar atoms or groups, the valence of which, however, is not required to be the same in the solid as in the liquid form of the elements concerned.

The more important contributions to each of these viewpoints will here be reviewed, and it will be pointed out that a simplified form of (3) is in the light of our present knowledge the only reasonable interpretation of the isomorphism of the plagioclases.

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[1] *Ber. Akad. Wiss. Wien,* **50**, 566, 1865.

No explanation of the isomorphism in question can be accepted if it does not account for the molecular volume relations, the practical non-replaceability of aluminium by iron, and the very limited isomorphism of orthoclase ($KAlSi_3O_8$) and carnegieite ($Na_2Al_2Si_2O_8$) with anorthite.

That the "molecular volumes" of empirical-formula amounts of albite and anorthite are identical has been recognized for so long that it is not certain who first pointed it out. The term molecular volume is somewhat of a misnomer, for it refers not to the volume of a single molecule, but to that of an amount of the substance measured by the formula weight in grams; "gram-formula volume" is therefore preferable. This is obtained by dividing the formula weight by the density. In the present instance the formula weights are not accurately known, for the atomic weight of aluminium may be anywhere between 26.95 and 27.10, that of silicon between 28.10 and 28.30; moreover, few workers agree on the densities beyond the first decimal place. Using average values, $NaAlSi_3O_8$ amounts to 262.7, and as the density of pure albite is 2.60, the g-f.v. is 101 cc.; $CaAl_2Si_2O_8$ amounts to 278.6 and the density of anorthite is 2.76, so its g-f.v. is the same as that of the preceding. As shown more particularly by Prior,[2] a similar relation holds in many cases of isomorphism between substances of apparently distinct formula type. Of course, identity of g-f.v. is not sufficient to explain a case of isomorphism, but it does point to the conclusion that the isomorphism in the plagioclases is based on a 1:1 ratio of empirical formula amounts of the two end-numbers, and that no explanation of it should be accepted which assumes any other ratio between them.

The non-replaceability of aluminium by iron in the feldspars is striking. Such ferric feldspars as have been made artificially are unstable, and in nature when any ferric oxide gets incorporated with a feldspar at the time of its crystallization it separates as inclusions of hematite. The gem orthoclase of Madagascar may be an exception to this rule, but it is nearly, if not quite, unique. On the other hand, in certain other silicates, as for instance garnet, epidote, and tourmaline, ferric iron appears to be able to replace aluminium readily and extensively. The well known instability of the ferrates as compared with the aluminates suggests that these relations are due to the fact that in the feld-

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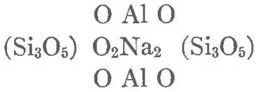
[2] *Mineralogical Mag.*, **13**, 217, 1903.

spars the aluminium is not basic as in garnet, etc., but belongs to the acid radicle, a view emphasized by Vernadsky[3] but not given the consideration it deserves by later writers.

Since the only difference between orthoclase and albite appears to consist in the replacement of one univalent metal by another, it would be expected that orthoclase would likewise be isomorphous with anorthite. Alling[4] suggested that this is the case, and named the series oranite, but he gave no data to show that such solid solutions of orthoclase and anorthite as may conceivably occur in nature are really of isomorphous character. The grouping of the hundreds of analyses he plotted seems on the contrary to indicate definitely that only limited, non-isomorphous solid solution exists.

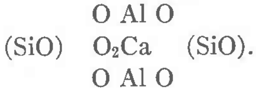
It might also be expected that carnegieite would be isomorphous with anorthite, since the chief difference between them consists in the replacement of two univalent sodium atoms for one bivalent calcium atom. That this is, however, not the case is shown by the extreme rarity and at best small carnegieite content of the feldspar anemousite, as well as by the careful synthetic experiments of Bowen,[5] whose determination that carnegieite holds only 5 per cent of anorthite and anorthite only 2 per cent of nephelite-carnegieite clearly indicates that these solid solutions are non-isomorphous.

(1) STRUCTURAL FORMULA INTERPRETATIONS.—In the paper of Vernadsky cited, the feldspars were regarded as underlain by a "mica nucleus," and from the description of this conception it would appear that he looked upon albite as something like



$$(\mathrm{Si_3O_5})\ \underset{\mathrm{O\ Al\ O}}{\overset{\mathrm{O\ Al\ O}}{\mathrm{O_2Na_2}}}\ (\mathrm{Si_3O_5})$$

and anorthite as



$$(\mathrm{SiO})\ \underset{\mathrm{O\ Al\ O}}{\overset{\mathrm{O\ Al\ O}}{\mathrm{O_2Ca}}}\ (\mathrm{SiO}).$$

Except for the aluminium being part of the acid radicles in both, the two formulas are quite different.

The structural formulas of Clarke[6] differ from the preceding ones in regarding aluminium as basic and not connected with the alkali or alkaline earth metals, albite being $\mathrm{Na\text{-}O\text{-}Si \equiv O_3 \equiv Si - O - Si \equiv O_3 \equiv Al}$ and anorthite $\mathrm{Al \equiv O_3 \equiv Si - O - Ca - O - Si \equiv O_3 \equiv Al}$.

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[3] *Z. Kryst. Min.*, 34, 60-61, 1901.

[4] *J. Geol.*, **29**, 193, 1921.

[5] *Am. J. Sci.*, **33**, 571, 1912.

[6] *U. S. Geol. Survey Bulls.* **125** and **588**.

He definitely accepted the two markedly dissimilar silicate radicles, (Si_3O_8) and (SiO_4), as mutually equivalent. This viewpoint is popular among American mineralogists, being, in spite of the considerable volume of literature on the subject herein cited, often the only one mentioned in discussions of the relationships between silicates, as for instance in the monograph on the feldspars by Alling. Clarke and others have used the assumed equivalence between these two silicate radicles to account for the excess silica in nephelite, micas, zeolites, etc. But in nephelite, at least, it has been clearly shown by Bowen[7] that the solid solution is limited and, therefore, presumably non-isomorphous; and the other instances can be equally well explained on various assumptions.

The structural formula viewpoint would appear to have reached its climax in the monstrous ring formulas of the Asches,[8] which may be passed over without further consideration.

As an anti-climax, Gossner[9] has written formulas for these minerals according to a pseudo-coördination plan, albite becoming $SiO_3Na_2\ (SiO_2Al_2O_3).4SiO_2$ and anorthite $SiO_3Ca\ (SiO_2AlO_3)$. He regarded these as very similar in type, but failed to note that the $4SiO_2$ is here isomorphous with nothing at all.

All of the plans of this group have the same failings. In the interest of having one bivalent calcium correspond to two univalent sodiums, they are willing to consider quite dissimilar acid radicles isomorphously replaceable, and to disregard entirely the gram-formula volume relations by making two albites equivalent to one anorthite. Except in so far as Vernadsky recognized the close connection between aluminium and the alkali or alkaline earth metals, they assign no reasons for the lack of replaceability between iron and aluminium, potassium and sodium, and one calcium for two sodiums in carnegieite. Such structural formulas are, therefore, quite inacceptable.

(2) ARITHMETICAL INTERPRETATIONS.—The valence-volume theory of Pope and Barlow[10] appears to represent essentially a generalization from the chance relation that tetravalent carbon sometimes occupies approximately four times the volume of

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[7] *Am. J. Sci.*, **33**, 49, 1912; **43**, 115, 1917.

[8] The silicates in chemistry and commerce, 1913.

[9] *Centr. Min. Geol.*, **1921**, 522.

[10] *J. Chem. Soc.*, **89**, 1675, 1906.

univalent hydrogen. It is quite unsupported by gram-formula volume data in general, and merits little attention. The total valence of both albite and anorthite is 32, as pointed out by these authors (p. 1727), but other silicates also have total valences of 32 and yet are not isomorphous with them.

The molecular compound viewpoint has been summed up clearly by Sosman.[11] According to it the oxides making up ordinary silicates (the feldspars were not mentioned specifically) tend to unite in simple numerical proportions regardless of structural formula relations, the resulting products being in a modern sense molecular compounds. On this basis albite would be $Na_2O.Al_2O_3.6SiO_2$, and anorthite $CaO.Al_2O_3.2SiO_2$, disagreeing with the gram-formula volumes in that albite is here doubled.

The isosterism viewpoint is an outgrowth of the octet theory of Langmuir.[12] Elements or radicles possessing like electron arrangement are regarded as capable of isomorphous equivalence even tho they are chemically apparently dissimilar. The available electrons in both albite and anorthite amount to 64, so as far as the whole formula amounts go, the two are alike. On the other hand, when the individual constituents are considered, it is found that calcium is isosteric with potassium but not with sodium, which would indicate anorthite to be more fully isomorphous with orthoclase than with albite, whereas actually the reverse is the case.

The chief objection to the viewpoints of this group consists in their failure to furnish any adequate explanation of the complexity of isomorphous relationships. If carried to their logical extreme, they would predict numerous cases of isomorphism which do not occur, practically requiring that the plagioclases should welcome replacement of one univalent, one bivalent, or one trivalent metal by any other with the corresponding valence, as lithium or potassium for sodium, strontium or barium for calcium, or ferric iron or chromium for aluminium; yet not one of these takes place. Arithmetical relations should be regarded as corollaries to, and not causes of, isomorphism.

(3) ATOMIC ISOMORPHISM INTERPRETATIONS.—By atomic isomorphism, as opposed to valence isomorphism, is meant the replacement of a single atom by one of another kind, irrespective of

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[11] *J. Ind. Eng. Chem.*, 8, 985, 1916.

[12] *J. Am. Chem. Soc.*, 41, 1557, 1919.

the valence exhibited by the same atoms in solution. This may be illustrated by the case of calcite and soda-niter, $CaCO_3$ and $NaNO_3$, which are so closely isomorphous that they form parallel overgrowths, whereas $CaCO_3$ and Na_2CO_3 are not isomorphous at all, and neither are $Ca(NO_3)_2$ and 2 $NaNO_3$. The structural formulas on the solution-valence basis would predict, on the other hand, that $Ca=O_2=C=O$ should be isomorphous with $Na_2=O_2=C=O$, but not with the structurally distinct $Na-O-N\equiv O_2$, and so on. It is of course possible to get around this by writing calcite as $(CaC)^{vi}\,O_3$, but this device does not really tell anything about the structure, although it does indicate double atomic isomorphism.

A viewpoint of this sort has actually been applied to the plagioclases, as mentioned by Groth,[13] and greatly extended by Washington.[14] Thereby albite becomes $(NaSi)^{v}\,(AlSi_2O_8)$ and anorthite $(CaAl)^{v}\,(AlSi_2O_8)$. This plan has the advantages of avoiding any necessity of assuming isomorphism between widely dissimilar acid radicles, and of corresponding to the gram-formula volume relations; but it does not account for the lack of replaceability of one atom by another of the same valence, and it implies splitting up of the atomic grouping in a manner for which there is no evidence.

One of the simplest methods of bringing out atomic isomorphism is the coördination plan of Werner,[15] which consists essentially of placing in brackets the dominant element of a compound together with such accessory elements or radicles as are firmly bound, and outside of the brackets more loosely bound ones. This plan has been applied to the plagioclases by Niggli[16] and Jakob,[17] although they unfortunately complicated matters by writing at least four different formulas of anorthite, ranging from $[SiO_6.SiO_2]\genfrac{}{}{0pt}{}{Al_2}{Ca}$ to $[Al(SiO_4SiO_2AlO_2)_3]\genfrac{}{}{0pt}{}{Al_2}{Ca_3}$, while albite became $[Al(SiO_4SiO_2SiO_2)_3]\genfrac{}{}{0pt}{}{Al_2}{Na_3}$. Niggli discovered, no doubt by patient research, that these formulations showed atomic isomorphism between Ca and Na and

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[13] Introduction to chemical crystallography, 1906, p. 85.

[14] *Am. J. Sci.*, **34**, 555, 1912.

[15] New ideas on inorganic chemistry, 1911.

[16] Lehrbuch der Mineralogie, p. 379, 1920.

[17] *Z. Kryst. Min.*, **56**, 299, 1921.

Al and Si. As, however, the relations between the constituents could be obscured equally well by various other modes of formulation on the coördination plan, it seems desirable to limit the choice of arrangements in some way.

DEVELOPMENT OF A SATISFACTORY INTERPRETATION.—From this review of the various explanations and their significance it is evident that any atomic isomorphism theory will account for the gram-formula volume relations of the plagioclases. The non-replaceability of aluminium by iron would seem to require, however, that the aluminium be definitely associated with the alkali or alkaline earth metal. The coördination plan is adapted to show this, an aluminium atom being regarded as dominant and given the central position, altho it is difficult to decide in the case of the feldspars which constituents are to be regarded as loosely bound and left outside the brackets. The extreme insolubility of albite, at least, suggests that all the constituents are so firmly bound as to deserve a place inside, giving $[\mathrm{Na\ Al\ (Si_3O_8)}]$, but there would seem to be no need of retaining the brackets at all. Albite then becomes simply $\mathrm{Na\mathbf{Al}\ (Si_3O_8)}$, and anorthite $\mathrm{Ca\mathbf{Al}\ (AlSi_2O_8)}$, atomic isomorphism being evident.

If it be inquired what sort of structure underlies these formulas, then in the absence of X-ray interpretation of the plagioclases, some suggestion may perhaps be obtained by comparison with the already cited instance of isomorphism between $CaCO_3$ and $NaNO_3$. The X-ray study shows them to possess the structure: $\equiv\mathrm{Ca}\equiv(\mathrm{C}\equiv\mathrm{O_3})\equiv$ and $\equiv\mathrm{Na}\equiv(\mathrm{N}\equiv\mathrm{O_3})\equiv$, the atomic as well as the valence isomorphism being complete. Calcium and sodium have lost such valence-dissimilarity as they exhibited when in solution and both have attained a valence (or pseudo-valence) of 6. Carbon and nitrogen, in solution presumably 4 and 5 valent, respectively, both become primarily trivalent in the crystal. In so far as the metal is united to the non-metal thru oxygen, the oxygen atoms have here become likewise trivalent. In other words, the valence relations in the solution merely limit the types of compounds which can crystallize out—preventing the development of $CaNO_3$ or $NaCO_3$ for instance—but do not continue to hold once the solid form is attained. If it is remembered that the suggestion is purely hypothetical, the inquiry may be answered by stating that albite might be something like $\equiv\mathrm{Na}\equiv(\mathrm{Al}\equiv\mathrm{O_3})\equiv(\mathrm{Si_3O_5})\equiv$, and anorthite $\equiv\mathrm{Ca}\equiv(\mathrm{Al}\equiv\mathrm{O_3})\equiv(\mathrm{AlSi_2O_5})\equiv$.

Finally, it remains to be considered whether the atomic isomorphism viewpoint is capable of furnishing any adequate explanation of the failure of orthoclase or of carnegieite to show isomorphism with anorthite. The modern geometrical theories of crystal structure, which are being in every respect confirmed by X-ray study, imply that atomic isomorphism should be the rule whenever the atoms concerned are so nearly equal in volume as to fit into the same geometrical arrangement. The calculations from the X-ray measurements made by W. L. Bragg[18] show sodium to occupy normally a volume very slightly greater than calcium, nitrogen but little less than carbon, and silicon similarly little less than aluminium. The two instances of isomorphism which have been discussed here are thus in entire accordance with the atomic volume relations. On the other hand, potassium occupies a decidedly larger volume than sodium or calcium; so potassium nitrate can not be expected to be isomorphous with calcite, nor orthoclase with anorthite. In the case of carnegieite, there are two sodiums for every calcium of anorthite, and the still larger volume required by these two atoms should make isomorphism even less possible.

It should be noted that there is no intention of claiming that valence isomorphism never occurs; for if a compound is sufficiently complex to have gaps in its geometrical structure, then two atoms may readily replace one of their own size by expanding into these gaps. This is the relation which has long been known as mass-isomorphism. All that is held is that valence isomorphism is not applicable to the plagioclases.

The atomic isomorphism viewpoint, in connection with the geometrical theory of crystal structure, is thus entirely capable of accounting for all of the relations observed in the plagioclase feldspars.

SUMMARY.—In this paper it is shown that the structural formula viewpoint is incapable of accounting for the isomorphism of the plagioclases, that the arithmetical viewpoint mistakes a corollary for a cause, and that only the atomic isomorphism viewpoint really corresponds to the data. As sodium is indicated by X-ray measurement to occupy approximately the same volume as calcium, and aluminium as silicon, the two feldspars may well have identical geometrical structures; the valence relations in solution merely require the one replacement to be accompanied by the other, and

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[18] Phil. Mag., **40**, 169, 1920.

do not persist into the solid form of the compounds. Orthoclase and carnegieite can not be isomorphous with anorthite because the potassium atom of the one, and still more the two sodium atoms of the other, demand more space than displacement of the calcium can furnish. The simplest formulas adapted to bring out all the relations are: Albite, $NaAl(Si_3O_8)$; anorthite $CaAl(AlSi_2O_8)$.

AUGITE AND HORNBLENDE FROM KILIMANJARO

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In the present paper are described some crystals of augite and hornblende which were collected in 1920 by Mr. Scott, of the Universal Film Company, on "the southeast slope of Kilimanjaro." Dr. W. F. Foshag, of the U. S. National Museum, kindly gave them to us for study and we acknowledge with pleasure our indebtedness to him for the opportunity to add a little to our scanty knowledge of the mineralogy of East Africa.

Little is known in detail of the rocks of Kilimanjaro. According to Hyland,[1] who studied a collection of rocks made by Mayer in 1887, there occur basalt obsidian, limburgite, nephelite basalt, feldspar basalt, tephrite, nephelite basanite with "rhomb" feldspars, and leucite basanite (the first leucite rock to be described from Africa). According to Meyer, in 1900, as cited by Reed,[2] the lavas are chiefly leucitic; while Jaeger[2] reports rhomb prophyry as most abundant, with trachyandesite, trachydolerite, and recent phonolite. There can be no doubt that the lavas of Kilimanjaro in general are dominantly sodic and not very high in silica; and that they resemble those of Kenya and the other volcanoes of the Ethiopian Rift Valley, as described by Prior[3] and others.

Augite

The crystals of augite were evidently found loose in ash, but there is no information as to the kind of lava from which they come. They differ in some respects from those described by Becker,[4] which were also loose crystals. The form and size of our augite crystals are the usual form and size for such augites. They

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[1] Hyland, J. S., *Tsch. Min. Pet. Mitth.*, **10**, 203, 1888.

[2] Reed, F. R. C., Geology of the British Empire, 1921, p. 75.

[3] Prior, G. T., *Min. Mag.*, **13**, 228, 1903.

[4] G. Becker, ref. in *Zeits. Kryst.*, **38**, 317, 1904.