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THE ISOMORPHISM OF ALBITE AND ANORTHITE¹

FERRUCCIO ZAMBONINI, *University of Naples*

ABSTRACT BY H. S. WASHINGTON, *Geophysical Laboratory,
Carnegie Institution of Washington*

INTRODUCTION

In the January (1923) number of THE AMERICAN MINERALOGIST Dr. E. T. Wherry has expounded his interesting and suggestive views on "Volume Isomorphism in Silicates," the fundamental idea being that atoms that have approximately equal volumes can replace each other "isomorphously," while those with widely different volumes cannot. Wherry minimizes the importance of valency in such isomorphous replacement and disbelieves in the necessity of equality in the sums of the valencies of the replacing atoms.

During the discussion of Wherry's paper I not only "called attention to the fact that Professor Zambonini is working along similar lines," as Dr. Wherry says in a foot-note, but stated that Zambonini's views regarding the relations of atomic diameters or volumes² to isomorphism are essentially identical with those of Wherry. I also commented on the interest that lay in the fact that two workers had independently and almost simultaneously arrived at almost identical conclusions, and remarked that this independent agreement was a strong point in favor of the probable correctness of the new explanation of certain cases of isomorphism.

Before beginning the abstract of Professor Zambonini's paper, I trust that I may be permitted a word of introductory personal explanation. In May, 1922, on the train between Naples and Rome, Professor Zambonini explained to me his theory at some length, and asked me to publish an abstract of his forthcoming paper in an American scientific journal, to which request I assented. He sent me later a separate of his paper whose title is

¹ F. Zambonini, *Rend. Accad. Lincei*, 31, 295-301, (April 23), 1922.

² Zambonini speaks in terms of atomic diameters, while Wherry uses atomic volumes; the fundamental ideas are the same.

given above, but unfortunately, the publication of the abstract was delayed. The publication of this abstract at the present time seems to be especially desirable, not only in justice to Professor Zambonini, and in fulfillment of my promise to him, but so that American mineralogists may be able to compare the views of Zambonini and Wherry, as the Italian journal is accessible with difficulty in this country. In the following abstract most of the paper will be summarized very briefly, but the more important passages will be given in full in literal translation.

THE ABSTRACT

In the first three pages Professor Zambonini discusses the isomorphism of albite and anorthite and the various explanations that have been advanced for the demonstrated isomorphism in spite of the difference in type of chemical formula of the two minerals. He calls attention to the observation of Hiortdahl³ that in certain cases of such isomorphism there is equality of the total valencies of the replacing elements, and he accepts the suggestion of Groth⁴ that in the change from albite to anorthite there is substitution of a group CaAl for the group NaSi, with equal sums of the principal valencies.

"We are dealing, certainly, with facts that do not enter into the ordinary isomorphous substitutions of "vicariant" elements, because in such cases an atom of calcium should replace two atoms of sodium, as is seen in so many minerals. Is it possible to give a plausible explanation of these singular substitutions, atom for atom, of elements of different valencies? I think that one can do so, if one takes into account the recent very important researches of W. L. Bragg⁵ on the arrangement of the atoms in crystals, from which he has been able to calculate the atomic diameter of the various elements.

"According to Bragg the atomic diameter of silicon is 2.35 Å and that of aluminum is 2.70 Å, the difference, as can be seen from Bragg's table, being of the same order of magnitude as differences between some atoms which are certainly "vicariant." One can thus understand how an atom of aluminum can take the place of one of silicon in the crystal structure of albite without bringing about notable change [in form].

³ T. Hiortdahl, *Zeits. Kryst.*, 12, 416, 1887.

⁴ P. Groth, *Chemische Krystallographie*, 2, 275, 1908. For an extended application of Groth's suggestion see H. S. Washington, *Am. J. Sci.*, 34, 555, 1912.

⁵ W. L. Bragg, *Phil. Mag.*, 40, 169, 1920.

"The conditions in the case of sodium and calcium are still more favorable, because the atomic diameters of these two elements are respectively 3.55 and 3.40 Å. The fact is also noteworthy that the smaller atomic diameter of calcium relative to that of sodium largely compensates for the difference between the atomic diameters of aluminum and silicon. In its entirety, the change from albite to anorthite takes place with a difference in the sum of the atomic diameters of only 0.2 Å, which is practically negligible if one considers that one is dealing with a complex of some thirteen atoms.

"An atom of aluminum can take the place of one of silicon, not only because of the small difference between the atomic diameters of the two elements, but also because aluminum presents some interesting relations with silicon. Aluminum is, in fact, a notably amphoteric element and it can thus assume the acid function which is played by silicon; besides which, and this is very important, aluminum is one of the two heterologues of silicon itself. To this combination of circumstances is due the power that aluminum has of replacing silicon, atom by atom, in certain silicates.

"The fact that the replacement, in the crystal edifice of albite, of an atom of silicon by one of aluminum is accompanied by the replacement of an atom of sodium by one of calcium is, in my opinion, of special interest, because it offers strong support to the ideas of those who believe that the forces which hold together the atoms in the crystal structures of many substances are comparable with the principal valencies. Indeed, we can think * * * * * that when we replace an atom of silicon by one of aluminum in the structure of albite, the eight oxygen atoms remaining fixed with their sixteen valencies, it necessarily happens, in order that all the valencies of the oxygen may be satisfied, that the atom of sodium must be replaced by one of a bivalent element, such as is calcium.

"The rule of Hiortdahl is, thus, explained. In compounds in which the principal valencies control, the sum of the valencies and the number of the atoms⁶ (or radicals) must remain unchanged in passing from one compound to another by substitution of atoms of different valencies, in order that the crystal form may not suffer great modification."

⁶ "It is necessary also, naturally, that the atoms which replace each other should present certain chemical and structural relations, otherwise the rule will not be followed. The condition that the number of the atoms should remain unchanged was not suggested by Hiortdahl."

In a note to a brief discussion of Langmuir's "Octet Theory of Valence" Zambonini says: "I must again insist on the fact that the particular nature of the atoms that replace each other is of essential importance in order that Hiortdahl's rule may be followed. The isosterism of Langmuir is not applicable: thus, Ca^{++} and Na^+ are not isosteric but, notwithstanding, albite and anorthite are isomorphous; while Na^+ and Mg^{++} are isosteric but a magnesium anorthite does not exist."

Zambonini brings up the isomorphism of diopside, $\text{CaMgSi}_2\text{O}_6$, and acmite, $\text{NaFe}^{''}\text{Si}_2\text{O}_6$, as an example analogous to that of albite and anorthite, pointing out that iron and magnesium have almost identical atomic diameters, 2.80 and 2.85 Å, respectively, and that the sum of the valencies of CaMg and $\text{NaFe}^{''}$ are equal. He also cites the case of isogonism between triphylite, $\text{LiFe}^{''}\text{PO}_4$, and olivine, MgMgSiO_4 , which was noted by J. D. Dana in 1854. In this last case the atomic diameters of magnesium and iron are almost the same, as we have seen, and also those of lithium and magnesium (3.0 and 2.85 Å, respectively), while phosphorus is one of the heterologues of silicon. Zambonini finally explains similarly the isomorphism of orthoclase and celsian, the atomic diameters of potassium and barium being, respectively, 4.15 and 4.20 Å, while those of sodium and calcium are 3.55 and 3.40 Å, so that albite and anorthite do not form an isomorphous series with celsian.

It will be seen from the above that Zambonini and Wherry are at one in attributing these cases of isomorphism to the close agreement in atomic diameters or volumes of the "vicariant" elements, but that Zambonini considers as well that equality of the sum of the valencies of the replacing elements is essential, a point which Wherry regards as negligible. In brief, Wherry regards such replacements as simply spatial, or, as he puts it, "connected with volume rather than valence relations," while Zambonini regards them as both spatial and involving the preservation of a balance of forces.

In this connection a statement by Wyckoff⁷ is of interest. Near the conclusion of a paper on the structure of crystals as shown by X-ray study he says: "Such structures as zinc sulphide depart so far from being closely packed arrangements of atoms that some sort of directional character to the forces of combination between

⁷ R. W. G. Wyckoff, *Jour. Franklin Inst.*, 191, 229, 1921.

their atoms seems necessary to account for their existence as stable groupings." These "directional forces," as appears from the preceding discussion by Wyckoff, are what he terms "valency bondings," so that it would appear that the X-ray study of crystal structure favors Zambonini's view, which implies control by valency, rather than Wherry's simpler, purely spatial one.

It would appear⁸ that Barlow and Pope⁹ were the first, or among the first, as far back as 1906, to suggest that isomorphism depended on the replacement of atoms of similar sizes, as well as on like valency.

STERRY HUNT AND THE THEORY OF THE PLAGIOCLASES

It may be of interest to American mineralogists to add that Zambonini, in another paper,¹⁰ calls attention to the fact that Sterry Hunt¹¹ antedated Tschermak by about ten years in considering the members of the plagioclase group as mixtures of isomorphous albite and anorthite, and that the feldspars intermediate between the extremes are not definite mineral species.

ON STRUCTURE AND ISOMORPHISM IN CRYSTALS

RALPH W. G. WYCKOFF, *Geophysical Laboratory,
Carnegie Institution of Washington*

In a recent number of *THE AMERICAN MINERALOGIST* an interesting paper¹ has appeared which states that "It now seems 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." An abstract² of a paper expressing similar ideas has also been published.

In the second paper^{2,3} it is considered that isomorphous replacement will occur when there is a balancing of the valences of the atoms concerned and when at the same time the volumes of the

⁸ Cf. J. N. Friend, *The Theory of Valency*, 175-181, 1915.

⁹ Barlow and Pope, *Trans. Chem. Soc.*, **89**, 1724, 1906.

¹⁰ F. Zambonini, *Rend. Accad. Lincei*, **31**, 341, (May 7), 1922.

¹¹ T. Sterry Hunt, *Am. J. Sci.*, **18**, 270, 1854; *Phil. Mag.*, **9**, 354, 1855. See also Hunt's *Chemical and Geological Essays*, 444, 1875.

¹ E. T. Wherry, *Am. Mineralogist*, **8**, 1, 1923.

² F. Zambonini [H. S. Washington], *Am. Mineralogist*, **8**, 81, 1923.

³ F. Zambonini, *Rend. Accad. Lincei*, **31**, 295, 1922.