

ISOMORPHOUS RELATIONS OF $MgSiO_3$ AND $AlAlO_3$ IN SILICATESA. N. WINCHELL, *University of Wisconsin.*

There seem to be numerous examples of a simple isomorphous relationship between $MgSiO_3$ and $AlAlO_3$ in silicates. Even in the simple molecule, $MgSiO_3$, the molecule $AlAlO_3$ may apparently enter isomorphously to a limited extent, such as, about 5 per cent in enstatite and 10 per cent or more in anthophyllite. In certain larger molecules, such as diopside, $CaMgSi_2O_6$, and the equivalent amphibole molecule, $AlAlO_3$ seems to be miscible to about the same extent. According to experimental work by E. Fixek¹ in the laboratory of Professor Doelter, $AlAlO_3$ may enter $CaMgSi_2O_6$ (as well as $MgSiO_3$) isomorphously to as much as 25 per cent. In analyses of natural augite and hornblende the tenor of alumina not combined with alkalis rarely exceeds 10 per cent, but apparently may reach 15 per cent in very exceptional cases. In still larger molecules such as akermanite, $Ca_2MgSi_2O_7$, alumina may replace the entire tenor of $MgSiO_3$, thus leading to gehlenite, $Ca_2Al_2SiO_7$; this fact has been established beyond question by the experimental work of Ferguson and Buddington² at the Geophysical Laboratory. In another large molecule, namely antigorite, $H_4Mg_3Si_2O_9$, the theory of Tschermak, which has long been accepted by mineralogists, generally, requires that $AlAlO_3$ replace $MgSiO_3$ to form a (continuous?) series to the mineral amesite, $H_4Mg_2Al_2SiO_9$, of the chlorite group. The writer has recently argued that the same kind of variation occurs in the micas,³ and his views on this point have been called in question by Hallimond.⁴ Of course, it is not certain that there is the same kind of variation in the micas that seems to be present in pyroxenes and amphiboles, is generally accepted in chlorites and is certainly present in melilites, but if it does not occur in micas it would seem necessary to re-examine the evidence for it in the other groups. Therefore the determination of the question as to the micas is of considerable importance.

¹ Doelter: *Hdb. Mineralchem.*, II, 1, 1914, p. 568.

² *Am. Jour. Sci.*, CC, 1920, p. 141.

³ *Am. Jour. Sci.*, CCIX, 1925, pp. 309-328 and 415-431; *Am. Mineral.*, XII, 1927, pp. 267-279.

⁴ *Mineral. Mag.*, XX, 1925, pp. 305-319 and XXI, 1926, pp. 25-34; *Am. Mineral.*, XII, 1927, p. 413.

It is obvious that analyses of pure muscovite have no bearing on the question since every one assigns the formula $H_4K_2Al_6Si_6O_{24}$ to that mineral. The problem is to determine the composition (or the mode of variation from muscovite) of the micas which Tschermak called phengites and described as characterized by a small optic angle and a high tenor of silica. A study of analyses of micas is sufficient to show that phengitic micas are also characterized by the presence of an appreciable tenor of MgO or (Fe, Mn)O or both. According to Hallimond's theory this RO replaces Al_2O_3 , while according to the writer's theory $MgSiO_3$ replaces $AlAlO_3$ in the muscovite formula.

The writer⁵ has previously called attention to the fact that Doelter⁶ gives twenty-one analyses of phengite and that not one of these analyses contains enough $K_2O + Na_2O + Ca_2O_2$ to satisfy the requirements of the theory of Hallimond. A few of them do contain enough alkalis to meet the requirements of the writer's theory, but most of them are old and probably inaccurate. It seems best, as suggested by Hallimond, to disregard these entirely.

The writer⁵ also cited three modern analyses of phengitic micas, as rich in the phengite molecule as he could find, and showed that these correspond well with his theory. This evidence is clearly not sufficiently convincing, since Hallimond⁷ disregards it entirely and argues that "an ideal test of the theories would consist in a series of recent analyses made by the same observer, upon materials selected with care and graduated from pure muscovite up to the highest available content of MgO"; he adds that "fortunately a series of this kind is available in the well-known research by Kunitz." The writer agrees that this plan has certain advantages which make it worthy of attention. It is obvious that any test of the writer's theory must be based upon computations which are in harmony with that theory. This point was evidently overlooked by Hallimond when he made the comment that such a study of the analyses of Kunitz indicates "no trace whatever of a progressive diminution in $K_2O:SiO_2$ as the magnesia increased." As a matter of fact the analyses of Kunitz⁸ lead to the results expressed in Fig. 1, when they are plotted on two coordinates, namely K_2O

⁵ *Am. Mineral.*, XII, 1927, p. 272.

⁶ *Hdb. Mineralchem.*, II, 2, 1917, pp. 418-431.

⁷ *Am. Mineral.*, XII, 1927, p. 413.

⁸ *N. Jahrb. Min., Beil. Bd. L*, 1924, p. 365.

+Na₂O+Ca₂O₂ and MgO+FeO+MnO as required by the theory of the writer, each coordinate assuming that the analysis is calculated to the condition SiO₂+TiO₂=600, as suggested by Hallimond. In the diagram the numbered points representing the analyses should lie along the horizontal line to confirm the theory of the writer. Nearly all of these analyses contain too much alkali to agree with either theory, but it is clear that their average position is along a line inclined at least as much as required by the theory of the writer.

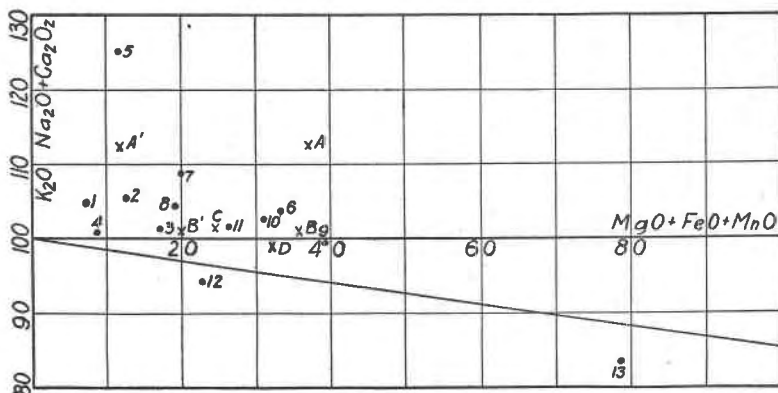


Figure 1. Relations between K₂O(+Na₂O+Ca₂O₂) and MgO(+FeO+MnO) in the muscovite system, assuming SiO₂+TiO₂=600, as shown by the data of Kunitz (*N. Jahrb. Min., Beil. Bd.*, L, 1924, p. 365). Nos. 1-11=Kunitz analyses 1-11 (*op. cit.*, p. 376); No. 12=Kunitz analysis 12, (*op. cit.*, p. 412); No. 13=Kunitz analysis (*op. cit.*, p. 383), his Fe₂O₃+FeO taken as FeO.

Of course this test is just as unfair to Hallimond's theory as his method of calculation is to the writer's theory. However, if the analyses are located by calculations based on the theory of Hallimond the only ones which would change position *materially* are numbers 5 and 7, which would then appear at the points A and B respectively. The average position of the points is then approximately along a horizontal line *with the very important exception of number 13*.

The difference in the two theories, so far as the method of calculation is concerned, is that Hallimond's theory requires that the CaO shall be included with MgO, while the writer's theory requires that it shall be included with the alkalis. Jakob⁹ has very recently con-

⁹ *Zeit., Kryst.*, LXII, 1925, p. 443.

cluded, after making many analyses of very carefully purified micas, that they contain no lime whatever, and that any lime found is due to impurities in the mineral sample or in the reagents used. If this is true, then analyses 5 and 7 belong at the points A' and B' respectively, and the average position of the points is then clearly along an inclined line similar to that required by the writer's theory.

There is one way to use the analyses of Kunitz to test the question which is fair to both theories. There are only two of his analyses that contain important amounts of lime. If these two analyses (Nos. 5 and 7) be removed from the diagram entirely, the remaining points¹⁰ show clearly the "progressive diminution in the $K_2O:SiO_2$ " ratio with increase of magnesia which Hallimond failed to find.

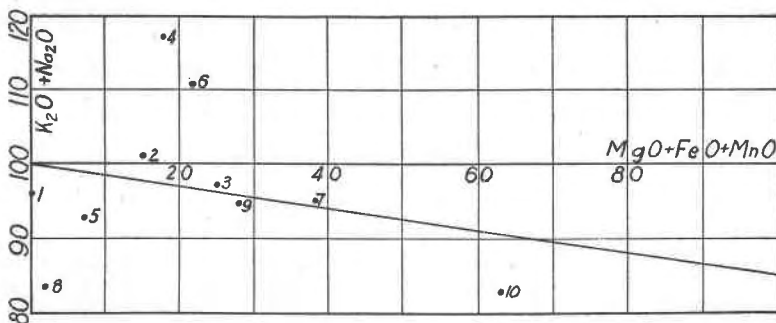


Figure 2. Relations between $K_2O(+Na_2O)$ and $MgO(+FeO+MnO)$ in the muscovite system, assuming $SiO_2+TiO_2=600$, as shown by the data of Jakob (*Zeit. Kryst.*, LXII, 1925, p. 443). Nos. 1-10=Jakob's analyses 9-18 in regular order.

On account of this difficulty as to the proper way to calculate the lime in order to test the two theories it is fortunate that there is another "series of recent analyses made by the same observer, upon materials selected with care and graduated from pure muscovite to the highest available content of MgO " which includes no lime whatever in any of the analyses. This is the series of Jakob.⁸ Calculations of the analyses of this series lead to the

¹⁰ Of the eleven analyses remaining, six contain no lime whatever, three (1, 4 and 9) contain less than 0.2 per cent, and two (8 and 11) contain about 0.4 per cent. Calculated by Hallimond's method analysis 8 appears at C and analysis 11 at D.

diagram¹¹ shown in Fig. 2. Some of the points on this diagram vary from the average position more than is to be expected, but, nevertheless, the mean position seems to be along a line inclined at least as much as required by the writer's theory.

The writer is gratified to learn from Dr. Hallimond's recent discussion¹² that he is ready to admit the presence of "small quantities of other molecules" in micas not having the constant ratio $K_2O:SiO_2=1:6$. The only question seems to be, then, whether these "small quantities" can become large quantities in some cases. It seems to the writer more reasonable to accept a small variation in the $K_2O:SiO_2$ ratio rather than to assume a large variation in that ratio such as would be necessary to explain the results of some analyses if one is to cling to the idea that the main part of every analysis consists of mica having the 1:6 ratio. If the $K_2O:SiO_2$ ratio varies only a little from 1:6, then, obviously, large quantities of such molecules must be present to explain the results of some analyses.

The chief theoretical difficulty with the theory of Hallimond that MgO replaces Al_2O_3 in muscovite is that it requires one to believe that one atom of magnesium may take the place of two atoms of aluminum, and that one atom of oxygen may take the place of three atoms of oxygen, in the crystal space lattice. The chief practical difficulty with the same theory is that it is not in harmony with the modern analytical data on the composition of micas of the muscovite series.

THE BLACK HILLS MINERAL REGION

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INTRODUCTION

There is probably no other region 100 miles long and 50 miles wide that contains such a wealth of geological and mineralogical interest as the Black Hills of South Dakota. The pegmatites in the region around Harney Peak have yielded a number of rare minerals, some being new species, and large amounts of many more common ones. There too are found the largest known crystals of

¹¹ An error must be corrected: in the writer's former article on the micas (*Am. Mineral.*, July, 1927), the "86 molecules" mentioned in the fourth line from the bottom of page 272 should read "91 molecules."

¹² *Am. Mineral.*, XII, 1927, p. 413.