

*The influence of chemical factors on the crystallization
of hornblende in igneous rocks.*

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IT is now more than sixty years since Tschermak first published his classical paper on the relationship between the pyroxenes and amphiboles,¹ but, in spite of our greatly increased knowledge of these important rock-forming minerals, many of the problems concerning their constitution and genesis remain unsolved. In particular, the nature of the conditions which determine whether a pyroxene or an amphibole will separate from a crystallizing magma are imperfectly understood, although the point is one of very considerable petrological significance. Much fuller information is necessary, particularly with regard to the relationship between the composition of the ferromagnesian minerals and the rocks in which they occur. The present paper merely represents a preliminary attempt to correlate the available chemical evidence and to determine what other possible factors might influence the character of the ferromagnesian crystallization.

It is very generally supposed that the concentration of the volatile components (water, &c.) in the magma determines whether hornblende or augite will crystallize out. This conception is based on several factors.

(a) The pyroxenes and hornblendes are metasilicates of magnesium, calcium, and iron, and, taken as a whole, the two groups are superficially rather similar both as regards chemical composition and crystallographic characters. For this reason they were considered to be dimorphous.

(b) The pyroxenes are of simple constitution and are anhydrous, whereas the hornblendes are chemically more complex and contain essential water, fluorine, &c.

¹ G. Tschermak, *Beziehung zwischen der Pyroxen- und Amphibolgruppe*. *Min. Mitt.*, 1871, p. 17.

(c) Amphibole does not crystallize from a dry melt in the same manner as pyroxene, but requires the presence of mineralizers.

(d) When hornblende is fused and allowed to crystallize it forms pyroxene plus a little magnetite, and does not simply recrystallize as the original amphibole.

(e) Amphiboles are characteristic of the deep-seated plutonic rocks which crystallized under pressure sufficient to retain the volatile components, whereas pyroxenes are typical of the rapidly cooled volcanic rocks from which most of the volatiles escaped during crystallization.

Actually, however, as pointed out by Eitel¹ and Kunitz,² the chemical similarity between the two groups is not nearly so close as Tschermak and his followers believed, but the resemblance is confined to the actinolite and cummingtonite series of the amphiboles. Some factor other than pressure and the concentration of the volatile components must control the separation of the minerals.

A similar view has been expressed by Niggli³ and by Bowen⁴ and is summed up by the former author in the following words: 'Es geht daraus mit Deutlichkeit hervor, dass die Frage, weshalb in einem Magma sich Augite statt Hornblendebilden, oft nicht nur eine Antwort vom physikalischen Standpunkte erheischt, sondern auch vom chemischen.'

The most suitable method of attacking the problem seems to be by a statistical comparison of the chemical compositions of the two groups, and, as shown below, this method leads to the conclusion that the ratios of the basic oxides in the magma are of primary importance in determining whether pyroxene or hornblende will separate from the melt.

The MgO-CaO-FeO ratios of the Pyroxenes.

Within recent years Asklund⁵ has published an elaborated survey of the crystallization courses of the pyroxenes and pyroxene-bearing rocks, based on a very complete statistical study of their MgO-CaO-

¹ W. Eitel, Die Mischkristallbildung in der Gruppe der alkali- und tonerdhaltigen Hornblendebilden . . . Neues Jahrb. Min., 1922, Beil.-Bd. 47, pp. 214-217.

² W. Kunitz, Die Isomorphieverhältnisse in der Hornblendegruppe. Neues Jahrb. Min., Abt. A, 1930, Beil.-Bd. 60, pp. 173-174. [M.A. 4-200.]

³ P. Niggli, Gesteins und Mineralprovinzen. Berlin, 1923, pp. 77-78.

⁴ N. L. Bowen, The evolution of the igneous rocks. Princeton, 1928, p. 91.

⁵ B. Asklund, Petrological studies in the neighbourhood of Stavsjö . . . Årsbok Sveriges Geol. Undersök., 1925, vol. 17, no. 6, pp. 75-88.

FeO ratios. This work, which represents a continuation and extension of the investigations of Wahl¹ and Sosman,² serves as a basis for the present comparative study, as regards the pyroxenes.

Both Sosman and Asklund were able to show that, among natural pyroxenes, an immiscibility gap exists between the diopside-hedenbergite series and the magnesia-rich, lime-poor monoclinic and ortho-

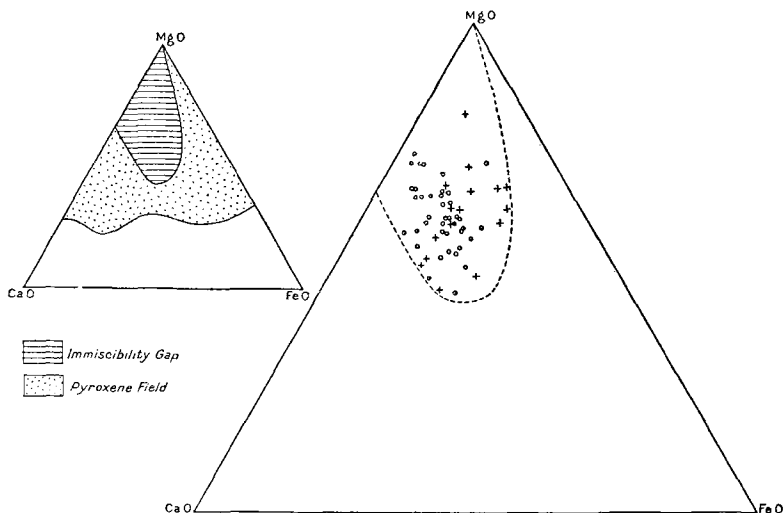


FIG. 1.

FIG. 2.

FIG. 1. Diagram showing the MgO-CaO-FeO ratios of the pyroxenes and metasilicate proportions of pyroxene-bearing rocks. (After B. Asklund.)

FIG. 2. Diagram showing the MgO-CaO-FeO ratios of igneous hornblendes (○) and metasilicate proportions of rocks containing hornblende as the sole ferromagnesian constituent (+).

rhombic pyroxenes. No points expressing the analyses of pyroxenes fall within this area and homogeneous pyroxenes of such composition do not exist in nature. This appears to be contrary to the results obtained by Bowen³ in his study of synthetic pyroxenes, for he found a complete series of mixed crystals in the system diopside-clinoen-

¹ W. Wahl, Die Enstatitaugite. *Min. Petr. Mitt.* (Tschermak), 1907, vol. 26, pp. 1-131.

² R. B. Sosman, Minerals and rocks of the composition $MgSiO_3$ - $CaSiO_3$ - $FeSiO_3$. *Journ. Washington Acad. Sci.*, 1911, vol. I, pp. 54-58.

³ N. L. Bowen, The ternary system: diopside-forsterite-silica. *Amer. Journ. Sci.*, 1914, ser. 4, vol. 38, pp. 207-264.

statite. It is significant, however, that, according to Wyckoff,¹ X-ray study suggests that diopside and clinoenstatite 'unmix' on cooling and give two patterns.

The relations of the natural pyroxenes, according to Asklund, are shown in the triangular diagram of the system MgO-CaO-FeO in fig. 1.² In the diagram, points expressing the compositions of single pyroxenes or rocks containing a single type of pyroxene fall outside the shaded area which represents an immiscibility gap in the system. Within this area no homogeneous mixed crystal has been found. On the other hand, points expressing the composition of a mixture of the two types of pyroxene or the metasilicate proportions of rocks containing two independent pyroxenes all fall within the immiscibility area. Thus, if the composition of a rock is such that it is represented by a point within the shaded area of fig. 1, its modal composition cannot be expressed by the crystallization of a single pyroxene, but only by the separation of two independent pyroxenes.

The MgO-CaO-FeO ratios of magmatic Hornblendes.

In order to effect a direct comparison between the magmatic pyroxenes and hornblendes it is evident that the latter must be subjected to the same method of treatment. This involves certain additional difficulties, however, for, as a rule, the hornblendes of igneous rocks contain greater proportions of sesquioxides than the aluminous pyroxenes and they contain also essential water. These factors would appear to invalidate any conclusions which might be drawn from such a statistical comparison.

In this respect, however, we must consider the role of Al_2O_3 in the constitution of the hornblendes. Warren³ has shown, as a result of his X-ray study of the amphiboles, that part of the alumina replaces silica in the structure and part replaces the MgO group. When allowance is made for these replacements in recalculating the analyses, it is found that the results differ little from those obtained by

¹ R. W. G. Wyckoff, Amer. Journ. Sci., 1925, ser. 5, vol. 10, p. 383.

² His method of calculation was as follows (loc. cit., 1923, pp. 75-78). In rocks containing femic silicates completely dominated by abundant pyroxene, the metasilicate proportions of the modal pyroxene were obtained by allotting CaO for anorthite, &c., and FeO for magnetite, &c. The remaining MgO, CaO, and FeO was then recalculated to 100, and the proportions obtained were plotted in the diagram. The same method was employed in the calculation of the analyses of pyroxenes.

³ B. E. Warren, Zeits. Krist., 1930, vol. 72, p. 493. [M.A. 4-278.]

Asklund's method, and the latter method of calculation is therefore valid.

The MgO-CaO-FeO ratios of forty analyses of igneous hornblendes,¹ together with the basic metasilicate proportions of sixteen hornblende-bearing rocks free from pyroxene and biotite, are plotted in the triangular diagram in fig. 2. It is seen that, without exception, *all the analyses fall within the area representing the immiscibility gap in Asklund's diagram for the pyroxene system.* The grouping is too regular to be fortuitous and must indicate the existence of some fundamental chemical relationship.

Although our knowledge is, as yet, incomplete the following tentative conclusions may be drawn :

(1) The MgO-CaO-FeO ratios of pyroxenes and magmatic hornblendes show marked and characteristic differences and, chemically, the latter appear to form a connecting link between the diopsidedhedenbergite series and the magnesia-rich, lime-poor monoclinic and orthorhombic pyroxenes.

(2) The ratios of the oxides in the original melt constitute a determining factor in the separation of pyroxene or hornblende. Rocks which have a composition represented by points outside the immiscibility area (hornblende field) cannot have hornblende as their sole ferromagnesian mineral.

(3) The influence of the volatile constituents is an unknown quantity, but, in some cases, it is found that changes in the ratios of the basic oxides lead to the precipitation of diopside in magmas saturated with respect to hornblende, although the concentration of the volatile components remains the same.² At the same time it is probable that any magma from which hornblende would crystallize under conditions tending towards the retention of the volatile components would, under effusive conditions (and with the escape of the volatiles), give rise to a mixture of two independent pyroxenes instead of a single pyroxene. The presence of water alone cannot therefore control the nature of the ferromagnesian crystallization.

¹ These represent the available analyses of hornblendes from igneous rocks quoted from the following sources :—C. Doelter, *Handbuch der Mineralchemie*, 1912-14, vol. 2 (I), pp. 586-649; H. Rosenbusch, *Elemente der Gesteinslehre*, 4th edition, 1923; W. Kunitz, *loc. cit.*, 1930, pp. 171-250.

² W. Q. Kennedy and H. H. Read, *The differentiated dyke of Newmains, Dumfriesshire . . . Quart. Journ. Geol. Soc. London (in the press).*