

The reciprocal role of alumina in reaction series.

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INQUIRY into this feature was stimulated by a reasonable doubt concerning the reality of the immiscibility gap in the clinoenstatite-diopside series. The existence of this gap was first suspected by Sosman¹ and Asklund,² and the identity of the gap with the composition field of the hornblendes has recently been suggested by Kennedy,³ whose comparative study of hornblende and pyroxene composition engaged statistical methods applied in the first instance by Asklund.

While this paper confirms and extends the findings of both Asklund and Kennedy, the latter author recognized the possibility that the statistical methods employed might, by reason of their arbitrary nature, invalidate conclusions based upon them.

Asklund's ternary diagram⁴ purports to show the MgO-CaO-FeO ratios of the pyroxenes and the metasilicate proportions of pyroxene-bearing rocks. But the quantities of these three oxides plotted in any particular case represent only a residuum of a full analysis from which alumina, ferric oxide, titania, and alkalis have been eliminated by allotments to normative compounds (anorthite, magnetite, &c.), though all these constituents (alumina, &c.) are liable to incorporation in both the pyroxene and the amphibole constitution. The fact that this method of computation did actually serve to detect the immiscibility gap is perhaps an index to the magnitude of the gap rather than to the cogency of the method itself.

¹ R. B. Sosman, *Minerals and rocks of the composition MgSiO₃-CaSiO₃-FeSiO₃*. Journ. Washington Acad. Sci., 1911, vol. 1, pp. 54-58.

² B. Asklund, *Petrological studies in the neighbourhood of Stavsjö . . . Årsbok Sveriges Geol. Undersök.*, 1923, vol. 17, no. 6, pp. 75-88.

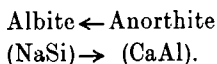
³ W. Q. Kennedy, *The influence of chemical factors on the crystallization of hornblende in igneous rocks*. Min. Mag., 1935, vol. 24, pp. 203-207.

⁴ W. Q. Kennedy, *loc. cit.*, p. 205, fig. 1.

Having regard to the results of X-ray work on the crystal-structure and constitution of both pyroxenes and amphiboles, the formulation of a pyroxene (or hornblende) composition in terms of empirical 'molecules' and their normative compounds is liable to obscure significant facts concerning mineral variation: atomic, as opposed to molecular, interplay is the mechanism of mineral change in general. The varietalism displayed by pyroxenes and amphiboles in particular is largely due to interplay between (*a*) atoms individually, e.g. $\text{Si} \rightleftharpoons \text{Al}$, $\text{Al} \rightleftharpoons \text{Mg}$, $\text{Mg} \rightleftharpoons \text{Fe}'' \rightleftharpoons \text{Mn}$, $\text{K} \rightleftharpoons \text{Na} \rightleftharpoons \text{Ca}$, &c., and (*b*) atom associations, e.g. $(\text{CaAl}) \rightarrow (\text{MgSi})$ in the progressive aggradation of metamorphic hornblende,¹ and $(\text{NaAl}) \rightarrow (\text{CaMg})$ accompanying the change actinolite \rightarrow glaucophane. This aspect of the case alone would discount the validity of Asklund's method, which nevertheless did reveal one linear dimension of the immiscibility gap.

In fig. 1, some hundreds of selected analyses have been plotted on an atomic basis: the polar terms are atoms—grouped consistently with their known replacement relationships. Of the three polar terms in Asklund's diagram, two (MgO and FeO) are accommodated, as atoms, at a single pole in fig. 1, which therefore reduces Asklund's diagram to a linear arrangement of points along the base-line of the figure, but supplies an additional co-ordinate engaging (AlFe''') atoms. Otherwise, the figure is self-explanatory, and serves to strengthen the case made out by Kennedy: the composition field of the hornblendes includes the immiscibility gap in the pyroxene series. Fig. 1 affords a convenient basis for an examination of the role of Al atoms in the two reaction series.²

In the continuous reaction series, the actual mechanism of reaction is the replacement of atomic Ca by atomic Na, and of atomic Al by atomic Si, i.e. $(\text{NaSi}) \rightarrow (\text{CaAl})$, while the initial pattern, or 'class' of crystal architecture, $n(\text{SiO}_2)$, persists unchanged. It may be expressed thus:



In the initial term anorthite, $\text{Ca}(\text{Al}_2\text{Si}_2)\text{O}_8$, one-half of the Si atoms are already replaced by Al atoms; but in the final term, albite, only one-fourth of the Si atoms are so replaced. Hence, progressive change in the sense anorthite \rightarrow albite implies the progressive elimination

¹ J. D. H. Wiseman, Quart. Journ. Geol. Soc. London, 1934, vol. 90, pp. 354-417.

² N. L. Bowen, The evolution of the igneous rocks. 1928, p. 60.

of Al atoms, and this change is graphically indicated in fig. 1 by the displacement of plagioclase evolutes *away from* the (AlFe⁺⁺⁺) pole.

Pari passu with this continuous change in the plagioclase series,

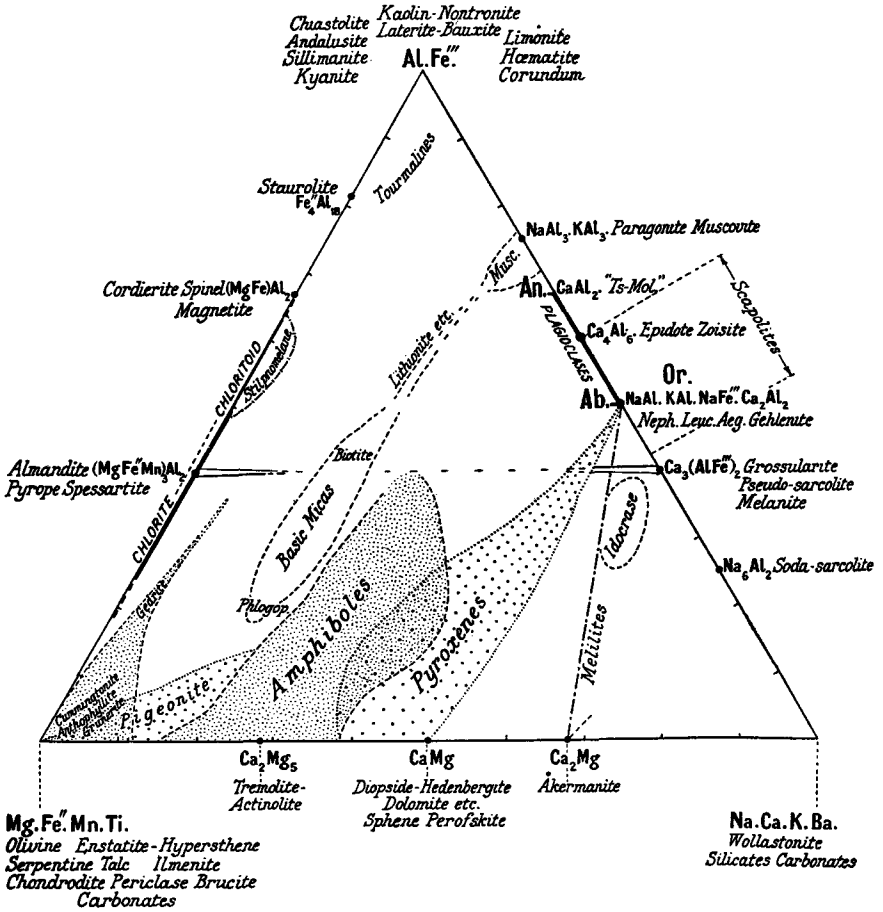


FIG. 1. Showing the composition fields for the chief rock-forming minerals. Some hundreds of carefully selected analyses are plotted on an atomic basis (in conformity with the results of X-ray work), silicon, phosphorus, hydrogen, &c., being 'in reserve'. This figure is reproduced from 'Science Progress', 1936, vol. 30, p. 619, and thanks are due for the loan of the block.

the discontinuous reactions proceed in the sense olivine → biotite (via augite and hornblende). These discontinuous changes are characterized by the enrichment of successive evolutes in (AlFe⁺⁺⁺) atoms,

succession being indicated by displacement *towards* the (AlFe^{III}) pole.

There is considerable warrant for the conclusion that the first Al atoms to gain access to the pyroxene constitution enter via the 'class'

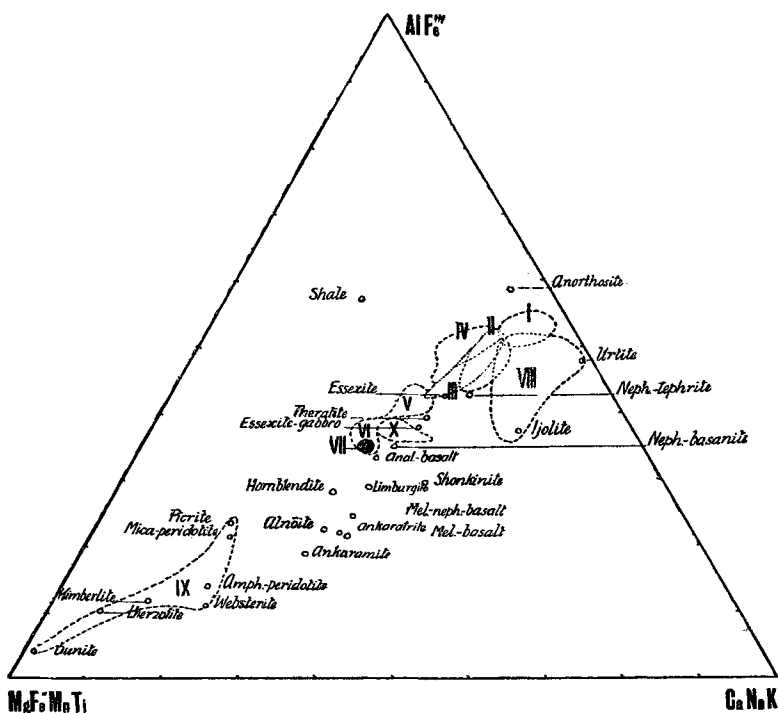


FIG. 2. Showing the composition fields for the main rock 'clans' (comprising both intrusive and extrusive types) and some individual rock types plotted from the 'average compositions' given in table I (pp. 9-28) of igneous rocks and the depths of the earth, by R. A. Daly, 1933. I, granites, &c.; II, quartz-monzonites, granodiorites, &c.; III, sub-alkali syenites, &c.; IV, diorites, tonalites, &c.; V, norites, &c.; VI, gabbros, &c.; VII, plateau-basalts, &c.; VIII, alkali-syenites; IX, ultrabasic rocks; X, lamprophyres.

group (or radix) distinctive of pyroxene structure, i.e. via the (SiO₃) group. This implies that Al atoms initially displace Si atoms; whereas in plagioclase evolution directed towards albite, Si atoms displace Al atoms. Hence the role of Al atoms in the two reaction series is in some manner reciprocal; but the feature is so intimately bound up with magmatic problems still at issue that discussion of

its implications here would involve tedious excursions into pure hypotheses.

It is as yet uncertain whether Al atoms acquired by an early-stage augite pass—by entail as it were—into derivative hornblende and biotite. Moreover, the constitution of the end-terms aegirine, riebeckite, and lepidomelane suggest that in the waning phases of magmatic crystallization, the effectiveness of the Al→Si replacement becomes enfeebled before the reaction Al→Mg, while enfeeblement of the latter is somewhat compensated by the displacement of Al atoms by Fe^{'''} atoms.

Reverting to the reciprocal role of the Al atoms in the two reaction series: this could be graphically illustrated by the swing of a compass-needle pivoted somewhere between the composition fields occupied by the two reaction series. The crystallization-differentiation theory would require that the pivot should itself be progressively displaced—from an initial 'station' in the ultrabasic or gabbroic field towards a granitic 'station', with numerous possible arrest points in the dioritic, granodioritic, monzonitic, syenitic, and other composition fields—each covering the entire 'family' (intrusive and extrusive terms included). As a matter of interest, an attempt has been made to determine approximate loci for these 'family' stations: on the reasonable assumption that Daly's 'averaged' analyses afford the best available basis for defining these composition fields, the whole of these analyses have been plotted in fig. 2, and the centres of the fields so defined may be regarded as the loci of the 'stations'.

The purpose of this paper is to call attention to certain relationships which, superficially at least, dovetail into each other, but when examined in the light of various rival theories concerning petrogenesis, lend themselves to a bewildering variety of alternative explanations.
