

pyroxene is from one of the igneous bodies which we have mapped, but there appear to be no other rock types in the area to which the published descriptions could apply.

The geological environments of the other two anomalous rocks also seem to provide the key to their interpretation. It appears likely that the "Olivine-bearing pyroxene granulite, Eilean Carrach, Ardnamurchan, Scotland" (Muir and Tilley, *op. cit.*, specimen R) is a thermally metamorphosed xenolith from the Hypersthene Gabbro of Centre 2. Although Richey and Thomas (1930, pp. 221–2) termed these rocks basic granulites, they imply that all these xenoliths were pyroxene-bearing igneous rocks. Similarly, the geological environment of the "Metamorphosed picrite basalt, ejected block, Kilauea" (Muir and Tilley, *op. cit.*, specimen X) is such that igneous conditions were dominant during its pre-explosive history.

It can be concluded that the geological setting of each of the three supposedly metamorphic rocks which have K_D values characteristic of igneous rocks (Kretz, *op. cit.*) is such that minerals characteristic of igneous rocks will be found. In the case of the rock from Scourie the pyroxenes are unaltered igneous pyroxenes, whereas in the rocks from Ardnamurchan and Kilauea, it seems likely that the pyroxenes are relict igneous pyroxenes or igneous pyroxenes reconstituted at igneous temperatures.

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CO-EXISTING PYROXENES

SIR.—In a recent issue of this magazine Dr. G. M. Brown made a revaluation of the existing data on tie-line orientation for co-existing pyroxenes in igneous assemblages. It was concluded that a precise point of intersection, at or close to $Wo_{75}En_{25}$ does not exist, and that, even given such a point hypothetically, its precise significance could not be easily explained. In arriving at this conclusion Dr. Brown used twelve analysed igneous pyroxene pairs. These included both orthopyroxene-augite and pigeonite-augite pairs, and were taken from six different igneous bodies.

While agreeing with Dr. Brown's general conclusions, the writer considers that as the tie-lines reflect the distribution of Ca, Mg, and Fe between two co-existing phases it is unreasonable to include the two different types of pairs, as orthopyroxene and pigeonite have differing crystal structures; furthermore the examples selected by Dr. Brown are from magmas cooled under differing conditions, and in which there may have been slight but

significant initial differences in composition which could affect element distribution between co-existing pyroxenes (De Vore, 1957) and hence affect the tie-line orientation. Kretz (1961), on the other hand, has concluded that variation in small amounts of Cr, V, Mn, etc., have little or no effect on the distribution of Fe and Mg and that the pressure dependence of the distribution is very small indeed, temperature dependence being the most significant factor.

Only in one intrusion, that of Skaergaard, have sufficient pigeonite-augite pairs been analysed to show their definite relationship in a single magma cooling with strong fractionation. Brown (1957) has published three analysed pigeonite-augite pairs taken from Skaergaard. One of these pairs (4385A) was separated by the writer who also analysed pigeonite-augite pairs from two further specimens closely comparable with 4385A. These later analyses, unpublished, prove to be very similar to the pair from 4385A but are included here for the sake of completeness (Table 1 and Text-fig. 1). When the tie-lines

TABLE 1

	1	1A	2	2A
SiO ₂	50.63	50.45	50.82	50.73
Al ₂ O ₃	2.71	2.04	2.46	1.55
TiO ₂	0.94	0.54	0.96	0.66
Fe ₂ O ₃	1.25	1.11	1.88	0.74
FeO	11.35	21.60	10.75	22.68
MnO	0.23	0.37	0.19	0.39
MgO	14.23	20.42	14.36	19.78
CaO	18.10	3.95	18.12	3.11
Na ₂ O	0.36	—	0.39	0.12
K ₂ O	0.08	—	0.03	0.05
TOTAL	99.88	100.48	99.96	99.81

1 and 1A augite and inverted pigeonite, specimen 4381.

2 and 2A augite and inverted pigeonite, specimen 4389.

The somewhat low Ca content of analysis 2A is probably due to the coarseness of the intergrowth in the inverted pigeonite, some of the intergrown augite having been separated from its orthopyroxene host during purification of the concentrates.

for all the Skaergaard pairs are projected it is seen that they intersect in a scatter which is very close to the point Wo₇₅En₂₅. For the Skaergaard pyroxenes the trend-line of augite co-existing with pigeonite is a straight line which passes close to, but slightly on the Ca side of, the Fe corner of the triangle; that is there is a slight bias in favour of replacement of the Mg over Ca by the Fe, and this bias remains constant during fractionation. The trend line of the pigeonite is likewise linear, but a constant Ca content indicates that only Mg, and not Ca, is replaced by Fe. Since the trends of co-existing augite and pigeonite are straight lines it is possible (see Appendix) to demonstrate that the condition which must hold for the tie-lines to meet at a point is that the curve of variation of iron content of the augite versus iron content of the pigeonite is one of a family of rectangular hyperbolas; the shape of the distribution curve will vary according to the location of the point of intersection of the tie-lines. It is relevant here to consider the work of Ramberg and De Vore (1951) relating to the distribution of an element between co-existing mineral pairs. Assuming that olivine and hypersthene are ideal mixtures, Ramberg and De Vore developed the following equation to relate the atomic ratio of magnesium in the two minerals:

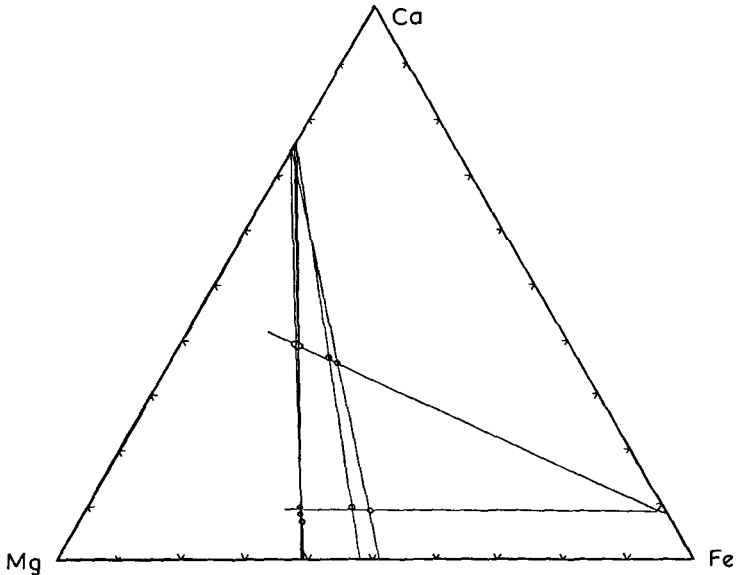
$$\frac{X_{\text{hyp}}}{1 - X_{\text{hyp}}} \cdot \frac{1 - X_{\text{ol}}}{X_{\text{ol}}} = e^{-\Delta F/2RT}$$

where $X = \frac{\text{Mg}}{\text{Fe} + \text{Mg}}$, T is the absolute temperature, R is the gas constant, and ΔF is the free energy of change of the reaction $\text{Mg}_2\text{SiO}_4 + 2\text{FeSiO}_3 \rightleftharpoons \text{Fe}_2\text{SiO}_4 + 2\text{MgSiO}_3$. Because ΔF is constant at constant temperature and pressure this equation may be written:

$$\frac{X_{\text{hyp}}}{1 - X_{\text{hyp}}} \cdot \frac{1 - X_{\text{ol}}}{X_{\text{ol}}} = \text{constant}$$

If this equation is to be satisfied then the distribution curve of Mg_{ol} versus Mg_{hyp} will be a rectangular hyperbola (see also Kretz, 1961, p. 369). Also the distribution curve may be expected to shift with change in temperature.

By similar reasoning it follows that if the augite and pigeonite series were ideal mixtures and if we consider the distribution of iron at constant



TEXT-FIG. 1.—Tie-lines joining five analysed augite-pigeonite pairs in the Skaergaard intrusion. The trend lines of co-existing augite and pigeonite are projected to the Ca-Fe join, disregarding the low Ca content of one of the pigeonite analyses. Fe is ferrous iron alone and does not include ferric iron or manganese.

temperature and pressure, then the distribution curve of Fe_{aug} versus Fe_{pig} will be a rectangular hyperbola. This is the special case considered by Kretz (1961), in which the distribution coefficient of iron will remain very nearly constant owing to the ratio Ca/Mg in both the augite and pigeonite remaining approximately constant over the range of crystallization considered. The family of rectangular hyperbolas required by the equation of Ramberg and De Vore is included in the distribution curves which must be followed by iron in co-existing augite and pigeonite if the tie-lines for those two minerals are to meet at a point on the Ca-Mg side of the triangular diagram. However, we are considering augite and pigeonite pairs co-existing as fractionation takes

place with declining temperature (pressure may reasonably be assumed to be constant). Wager (1960) has made the point that in the fractional crystallization of the Skaergaard magma 80 per cent of the magma was crystallized over a temperature range of only about 50° C. That the Skaergaard tie-lines for augite-pigeonite pairs do, to a close approximation, meet at a point would seem to indicate that the range of crystallization considered took place over a limited range of temperature which did not effect a significant shift in the distribution curve, and also that the augite and pigeonite series approximate to ideal mixtures.

It is possible that slightly different curves of iron distribution between co-existing pyroxenes may be found in different intrusions; furthermore, it must be noted how susceptible the tie-line orientations are to even small analytical errors in Fe or Mg.

It will be noted that as crystallization proceeds the ratio Fe augite/Fe pigeonite becomes progressively greater. Probably the main factor which influences the affinity of augite of iron is the calcium content, a decrease in calcium content of the augite increasing the structural affinity of that mineral for iron.

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APPENDIX

Let x , y , z represent the iron, calcium, and magnesium components of the pyroxenes as represented on the triangular diagram. Then $x + y + z = 1$. The Ca-poor pyroxene has constant calcium content, say k . It is hence represented by the line $y = k$.

The augite is also represented by a straight line which we can assume to be given by $y = a - bx$ where a , b are known (positive) constants.

Now, let u , v be the respective iron fractions in co-existing pigeonite and augite. Then these two forms are represented on the triangular diagram by the points $(u, k, 1-u-k)$, $(v, a-bv, 1-a(b+1)v)$. The join of these points is the tie-line for the co-existing minerals. The equation representing this tie-line is:

$$\frac{v-k}{x-u} = \frac{a-bv-k}{v-u}$$

Suppose now that all the tie-lines pass through a fixed point say $(X, Y, 1-X-Y)$. Then, for all pairs of values u, v ,

$$\frac{Y-k}{X-u} = \frac{a-bv-k}{v-u}$$

i.e. $buv - (a-Y)u - (Y-k+Xb)v + X(a-k)$.

This equation represents the variation of v with u , that is the variation of iron content of the augite with iron content of the pigeonite. It may be written:

$$\left(u - \frac{Y-k+Xb}{b}\right) \left(v - \frac{a-Y}{b}\right) = -\frac{X(a-k)}{b} + \frac{(a-Y)(Y-k-Xb)}{b^2}$$

which represents, for different values of X, Y , a family of rectangular hyperbolas.

When $X=0$ the tie-lines intersect on the Ca-Mg join and we have:

$$\left(u - \frac{Y-k}{b}\right) \left(v + \frac{Y-a}{b}\right) = -\frac{(Y-a)(Y-k)}{b^2}$$

When $Y=a$

$$v \left(u - \frac{a-k}{b}\right) = 0$$

This equation represents two perpendicular lines,

$$u = \frac{(a-k)}{b}, v = 0$$

When $Y = \infty$ (i.e. the tie-lines are parallel to the Ca-Mg join) then $v = u$. The major axis of symmetry of the hyperbola when $X=0$ is given by:

$$v = -u + \frac{a-k}{b}$$

This line passes through the point $\left(\frac{a-k}{b}, 0\right)$ in which the two perpendicular lines intersect when $Y=a$.

REVIEWS

- PALEOGEOLOGIC MAPS. By A. I. LEVORSEN. pp. 174 with 102 illustrations. W. H. Freeman and Co., San Francisco and London, 1961. Price 43s.
- LITHOFACIES MAPS: AN ATLAS OF THE UNITED STATES AND SOUTHERN CANADA. By L. L. SLOSS, E. C. DAPPLES, and W. C. KRUMBEIN. pp. xviii + 108, with 153 maps. John Wiley and Sons, Inc., New York and London, 1960. Price 44s.

Here are two books concerned with maps used in the interpretation of conditions during some geological episode.

PALEOGEOLOGIC MAPS are defined as representations of the geology of an area at some past time. A complete succession of such maps would then sum up a very large part of what geologists want to know—indeed to achieve this requires the deployment of full geological resources and experience and is not just a device from the drawing office. Thus while the book could be slimmer still if the object were to show what such maps are and how they can be made to work, there is no limit to the scope if positive results are intended. On the one hand the author defines and illustrates commonly used kinds of maps, and on the other he chooses specific examples and becomes involved in the discipline of regional and historical geology.

A book of this degree of specialization and cost is obviously not aimed at the elementary student and so the explanations of which kinds of maps show what will be primarily of interest because of the attempt to define and systematize an already familiar field. From this point of view the attempt is