

Calc-silicate skarn veins in the limestone of Lough Anure, Co. Donegal.

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INTRODUCTION.

A REMARKABLE series of wollastonite-garnet-idocrase veins occurs in the limestone quarries of Lough Anure in the Thorr area of Donegal. This locality lies on the extreme south of the one-inch Geological Survey of Ireland Sheet no. 9, and on the six-inch O.S. Sheet no. 41. S.E. In this area large isolated relics of Dalradian sediments are surrounded by a quartz-diorite which is highly modified at the contacts. This complex is intruded by an alkali-granite. The relict masses may be roof pendants or enclosures, and they are certainly structurally related to one another. It is the purpose of the present paper to describe the mineralization of one particular set of veins in a limestone forming part of one of the masses and exposed in two quarries about 300 yards SW. of the Lough Anure Technical School.

The area was surveyed by the Irish Geological Survey during the years previous to 1889, the mineralogy being recorded in the Memoir to Sheet 9 (1). Previous to this official survey, the main mineralogical contribution was that of Scott (2). In these and other works many references are made to calc-silicate minerals, but no details are given of the type of wollastonite-idocrase-garnet association described below.

OCCURRENCE.

The limestone of the quarries is a light grey, rather coarsely crystalline marble. It has darker bands indicating the bedding planes, and these dip at very low angles to the south. To the north-west the limestone appears to pass downward into a sillimanite-biotite-hornfels containing a sill-like mass of epidiorite; these beds are in contact with a cross-cutting biotite-rich granite. In small exposures near the granite, calc-silicate bands are common in the bedding planes, but in the pure limestone such minerals are confined to the margins of cross-cutting dikes and veins.

Exposed in the eastern quarry is a granitic dike which strikes E.-W. and dips steeply N. As is common with many of the minor intrusions of this area, a band of pegmatite is developed on the hanging wall. The dike has a sheath of calc-silicate minerals, of which garnet and idocrase are the most important species. One narrow cross-cutting dike, besides being enclosed by a sheath of calc-silicates, sends off numerous thin apophyses along the bedding planes, and these pass, within a short distance, into idocrase-garnet veins. Associated with the dikes are smaller veins characterized by a wollastonite-idocrase-garnet assemblage in which the wollastonite forms an outer zone as illustrated in figs. 1, 4, and 7.

These veins vary in composition from a mere whitened limestone to calc-silicate assemblages. Such extremes are present together in the western quarry where a thick, heavily mineralized vein dips steeply N. 36° W. In the immediate neighbourhood of the veins the limestone is whitened in broken streaks which conform to a structural pattern of two planes, one dipping at 40° N. 240° W., and the other steeply N. 105° W. Only in the strike of the first of these planes is there any relationship to the present joint system. In the eastern quarry some veins probably connect with the pegmatitic top of the dike.

The main dike is somewhat boudinaged and the smaller dikes and veins are gently folded and contain minute tension cracks. It can be shown that a late tectonic phase of minor importance affects the area.

MINERALOGY.

The chief minerals of the skarn veins are wollastonite, grossular, idocrase, diopside, and tremolite. The properties of each of the last four species vary slightly and therefore the determinations recorded below were made on minerals in juxtaposition. The wollastonite occurs in a white fibrous form often with a radiating structure; cleavage parallel to (100) is evident and twinning parallel to (100) is frequent. Laths showing cleavage traces exhibit a very small extinction angle, showing that the optic axial plane is slightly inclined to the axis of the cleavage zone. This fact is discussed by Peacock (3), who shows that the wollastonite of skarns is triclinic. The refractive indices are α 1.619, γ 1.634, the optical sign is negative, and the specific gravity 2.86.

The garnet is a flesh-coloured variety and occasionally shows striated (211) faces; it is completely isotropic, with a refractive index n 1.753 and a specific gravity of 3.56. These properties indicate an approximate composition of $\text{Gr}_{88}\text{And}_{12}$.

Idocrase occurs as yellowish-brown striated octagonal prisms with the following optical properties: ω 1.706, $\omega - \epsilon$ 0.006, uniaxial negative sign; pleochroism noticeable in thick section, ϵ faint yellow, ω colourless; zoning frequent; the specific gravity is 3.39.

Small crystals of a greenish diopside show the characteristic cleavages and have a refractive index γ 1.701, $\gamma - \alpha$ 0.29; biaxial positive sign with 2V moderate and $\gamma:c = \text{ca. } 39^\circ$. A green chlorite fills cleavage-cracks in the mineral. The optical properties are comparable with a diopside of the approximate composition $\text{Di}_{90}\text{He}_{10}$.

Fibres of slightly greenish tremolite have a refractive index γ 1.631, $\gamma - \alpha$ 0.026; biaxial negative sign with 2V large and $\gamma:c = \text{ca. } 19^\circ$.

Brownish pleochroic sphene showing its characteristic form is associated with diopside and idocrase in one of the veins, and it is interesting to note that this mineral is a typical accessory in the granite of the area.

This simple mineralogy is in contrast to that of other calc-silicate localities in the area, where epidote and other minerals enter the suite. These latter occurrences are found at the gradational junction of limestone, and pelitic sediments in proximity to the granite and their formation is influenced by the bedding planes.

PETROLOGY.

The limestone consists of a grey equigranular aggregate of calcite containing disseminated specks of graphite, many of which show hexagonal form. Occurring less abundantly are small flakes of white mica, grains of quartz, and a few scattered grains of epidote. Darker bands contain a greater abundance of graphite and mica with scanty pyrite. The amount of these impurities is variable, ranging, at least, from 10 % in a limestone with many dark bands to over 3 % in the more normal type. On partial analysis a typical grey limestone gave the following composition:

TABLE 1. Partial analysis of Lough Anure limestone. The insoluble residue obtained by treatment with hydrochloric acid consists in the main of graphite, muscovite, and quartz, together with a much lesser quantity of yellowish pleochroic epidote and a magnesia-mica.

Partial chemical analysis.				Calculated modal analysis.		
			%			%
CaO	50.56	Calcium carbonate	...	90.20
MgO	2.90	Magnesium carbonate...	...	6.25
Acid insolubles	3.20			

The period of regional metamorphism and injection which preceded emplacement of the late granite was responsible for recrystallization and formation of graphite from carbonaceous matter. Calcite and silica remained uncombined in this presumably deep-seated environment.

The granite dikes are later than the surrounding modified granodiorite and are petrologically similar to the late alkali-granite. They consist of microcline, albite-oligoclase, quartz, and brown biotite. The smaller dikes are richer in microcline, and accessory calc-silicate minerals such as diopside, garnet, and sphene occur instead of biotite. Granite-pegmatites associated with limestone and containing calc-silicates have been noted and discussed by several writers including Eskola (4), Read (5), Osborne (6, 7), and von Eckermann (8).

Minor cataclasis is shown by granulation and suturing of grains in the main granite and the dike series, and is consistent with the phenomena of minor tension cracks, boudinage, and foliation already noted.

The skarn veins fall into two categories; those with and those without a central magmatic dikelet. The former are confined to the eastern quarry and are probably connected with the pegmatitic top of the main granite dike. Typical examples of each type are described below to illustrate the main features of these veins, which are as follows:

- (A) The removal of graphite from the grey limestone in proximity to a quartz vein.
- (B) The formation of zones of calc-silicate minerals adjacent to a quartz-felspar vein.
- (C) The occurrence of calc-silicates both as an enveloping sheath and as accessory minerals in a plagioclase-microcline dike.
- (D) The occurrence of a thick skarn vein without a central magmatic dikelet, but with a much greater development of idocrase and grossular.

A. *The removal of graphite.*—The most conspicuous result of all the veining is the whitening of the grey limestone. This is especially well exhibited by one of the small veins, near which a sharp demarcation exists between grey and whitened limestone; this is shown in fig. 1. The vein is 1.5 mm. in width and consists of quartz containing minute calcite granules with a string of isotropic garnet grains forming a central portion and recrystallized calcite in the fork. Quartz-filled re-entrants which protrude into the limestone on either side contain both diopside and calcite granules. Small xenoblastic grains of diopside are present in both white and grey areas of the limestone. The amount of the mineral is, however, no more than could have resulted from combination of original silica and magnesia, and no appreciable maximum is shown in its concentration.

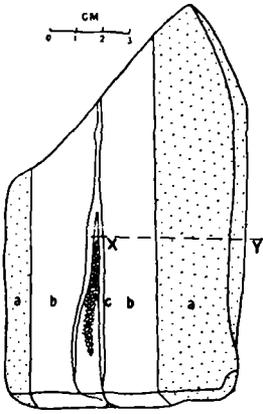


FIG. 1.

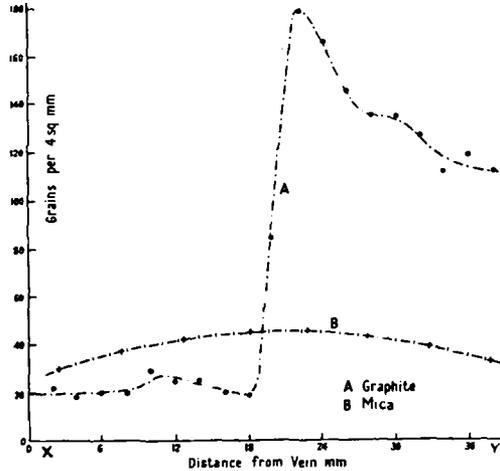


FIG. 2.

FIG. 1. Crystalline limestone with bifurcating quartz vein and showing sharp boundaries of zone free from graphite. *a*, grey graphitic limestone. *b*, white limestone. *c*, quartz vein.

FIG. 2. Count of mineral grains per 4 square mm. across wall-rock. Section XY of fig. 1.

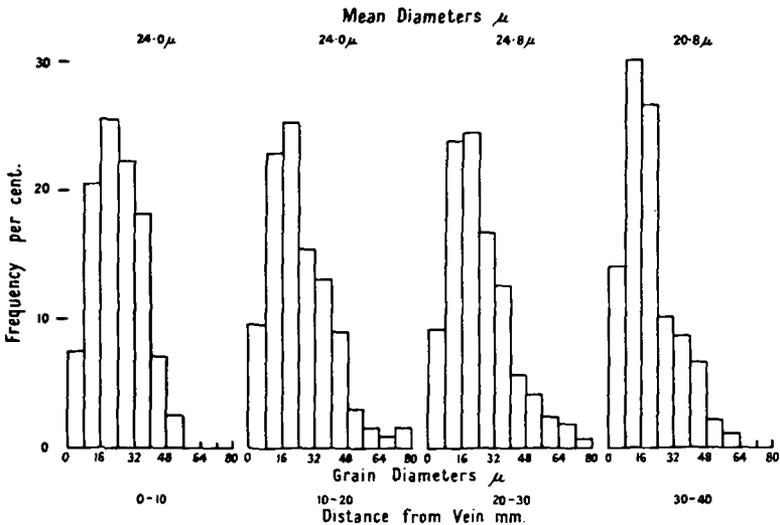


FIG. 3. Histogram showing the frequency per cent. of graphite grain-sizes at intervals across wall-rock of vein shown in fig. 1.

The graphite granules are found to be concentrated at the sharp demarcation line, as can be clearly seen from the graph of fig. 2. Comparison of the size frequencies of the graphite granules (fig. 3) shows that there is an increase in the frequency of the larger sizes immediately beyond the culmination point, with a corresponding increase in mean

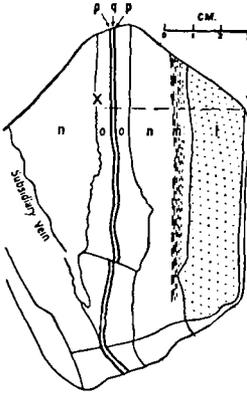


FIG. 4.

FIG. 4. Crystalline limestone with quartz-felspar vein showing bordering zones of calc-silicates. *l*, grey limestone. *m*, tremolite zone. *n*, diopside zone. *o*, wollastonite zone. *p*, idocrase sheath. *q*, quartz-felspar vein.

FIG. 5. Count of mineral grains per sq. mm. in a section of normal thickness across wall-rock of vein. Section XY of fig. 4.

A, graphite grains. B, quartz and muscovite. C, tremolite. D, diopside. E, limit of wollastonite. F, idocrase sheath to vein.

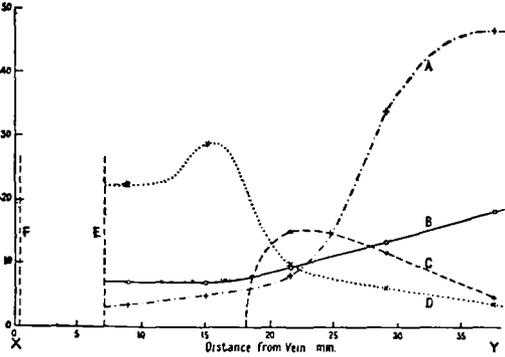


FIG. 5.

diameter. This latter factor is seen to have higher values within the affected zone than in the outer limestone. These facts indicate that the maximum shown by curve A, fig. 2, would be accentuated if it could be corrected to represent more nearly the true volume of graphite, and it is thus likely that the amount of graphite removed is approximately the same as that in excess of the normal concentration at the culmination point. Little, if any, graphite has been removed from or added to the system. The mica flakes, which are of similar size and shape to the graphite particles, are only slightly concentrated, and it would, therefore, appear that a purely mechanical explanation of the movement of the graphite is not feasible. The average size of the calcite granules is constant and there is no evidence of recrystallization at any appreciable distance from the vein, though this has occurred between the bifurcation shown in fig. 1.

B. *The presence of calc-silicate zones.*—A second case of skarn formation is that shown in fig. 4, in which a cross-cutting vein, 2 mm. in width and consisting of orthoclase, plagioclase, and quartz is bordered by crustified idocrase which has a replacement relationship towards an outer zone of wollastonite (fig. 6c).

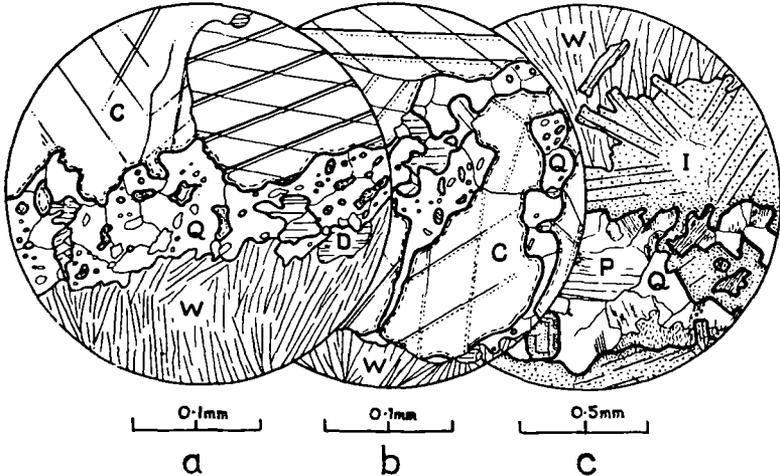


FIG. 6. Central portions of skarn vein, fig. 4.

- (a) Calcite-wollastonite boundary with intervening quartz selvage containing calcite granules.
 (b) Penetration of quartz along grain boundaries of calcite.
 (c) Central portion of vein showing idocrase replacing wollastonite. Well-formed crystals penetrate into the plagioclase-quartz dikelet.
 C, calcite. D, diopside. I, idocrase. P, plagioclase. Q, quartz. W, wollastonite.

The wollastonite forms a band on either side, averaging 5 mm. in width and with fibres approximately perpendicular to the vein. At the sharp junction between this mineral and the calcite there is a thin selvage of quartz containing granules of calcite and some wollastonite (fig. 6a); this is especially well developed where there are inter-granular projections into the limestone (fig. 6b), but here diopside is formed instead of wollastonite. There is no similarity between the opposite wollastonite-calcite boundaries, and it is reasonable to assume that the wollastonite is a result of a reaction between the limestone and silica introduced from the vein. The quartz containing the calcite granules is thus the result of 'freezing' the well-known reaction $\text{CaCO}_3 + \text{SiO}_2 \rightleftharpoons \text{CaSiO}_3 + \text{CO}_2$. With assumptions as to the pressure this will determine an isotherm in the heat exchange between the vein and the wall rock.

As in the first case described above there is a whitened zone quite sharply demarcated from the grey limestone, and the distance of this demarcation from the quartz selvage is approximately the same in both cases (23 mm.). The whitened area of limestone contains two mineral zones, an inner one containing granular diopside and an outer containing fibrous tremolite. This latter zone is shown as a narrow greenish band in the specimen illustrated in fig. 4 and is approximately 22 mm. from the centre of the vein. The diopside persists within the band of wollastonite, but exhibits a sharp decrease in concentration at a distance of 17 mm. from the vein (fig. 5). Beyond this point the concentration of tremolite rises rapidly to a maximum and then falls more gradually outward from the vein. In the very outermost zone examined, small fibrous aggregates of a moderately birefringent mineral occur, often as a reaction rim to grains of a greenish mineral which is probably a chlorite.

The quartz shows a decrease *pari passu* with silicate formation, and quartz grains in outer zones commonly contain acicular tremolite. The sequence of mineral zones is thus—idocrase and wollastonite, diopside, tremolite, and magnesia-poor limestone containing free quartz and graphite.

C. *Occurrence of accessory calc-silicates.*—Some of the thicker felspathic dikelets also develop sheaths of wollastonite, diopside, and bleached limestone, and in this type it is the magmatic portion which is of interest. One of the dikes, essentially composed of microcline, orthoclase, a lesser amount of plagioclase, and a little quartz, contains abundant idiomorphic diopside, brownish sphene, and small needles of apatite. Towards the contact with the bordering skarn, the dike contains fragments of calcite fringed with calc-silicates; idocrase becomes a common constituent and may be accompanied by a little zoisite. Considerable addition of lime has evidently been made to the intrusion both by incorporation of calcite and by reciprocal exchange of lime for silica.

Outward from the centre of the dikelet the felspars become increasingly turbid until they are nearly opaque at the contact; this alteration is due to the presence of minute moderately birefringent flakes, possibly produced at the time of silicate formation by a process akin to kaolinization.

D. *The thick skarn veins.*—In the principal skarn vein of the quarry, mineralization is intense (fig. 7). As in the above types, there is an outer zone of bleached limestone with diopside, but the wollastonite zone is

more variable in thickness, and at the junction with the limestone the calcite is often recrystallized in relatively large grains.

In this case no quartz selvage is present at the wollastonite boundary, where the marginal re-entrants and relict areas of calcite leave little doubt that the silicate has replaced calcite. Idocrase and garnet form a

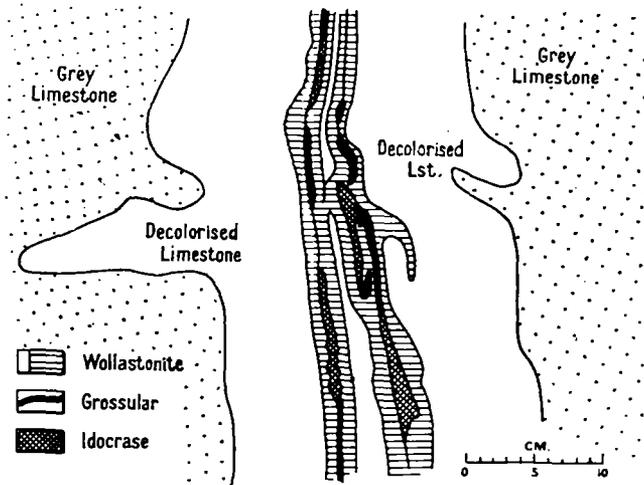


FIG. 7. Sketch of main calc-silicate skarn vein. Western quarry, Lough Anure. Vertical section.

central portion with relict areas of calcite and wollastonite, and here there is no plagioclase-quartz veinlet. The zoned idocrase contains residual fibres of wollastonite, diopside granules, and relict areas of calcite. Small areas of quartz are present, bordered by euhedral idocrase; the former mineral seems to have been released by the replacement of wollastonite by the aluminous calc-silicates.

The relationship in time of the garnet and idocrase is more difficult to assess. Contained within the garnet are relict areas of idocrase characterized by optical continuity and the identity of zonal bands; less commonly relics of garnet are present in the idocrase. Bearing in mind the similarity in structure between the two minerals, their intimate relationships are interpreted as evidence of simultaneous formation (fig. 7).

A feature of this particular skarn vein is the concentration of diopside granules in a line parallel and very near to the wollastonite-calcite boundary. The intervening calcite contains many less granules than the outer limestone, and this particular concentration is interpreted as a

sweeping outwards of impurities during recrystallization of the calcite adjacent to the vein. This mechanical effect is thus seen to be of small importance even where mineralization has been most intense.

DISCUSSION.

The removal of graphite.—The most striking effect of the action of the introduced material is the removal of carbon from the limestone in its immediate vicinity with a resultant piling-up of graphite beyond a knife-sharp demarcation line. This decolorizing effect is well known, though the resulting concentration near the vein may not be so widely recognized.

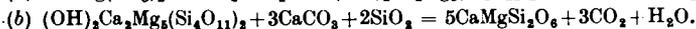
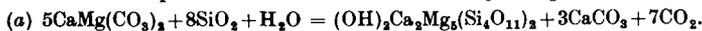
A hypothesis of simple distillation cannot be entertained, for the carbonaceous material was almost certainly graphitic at the time of the intrusion of the granite dikes. The fact that the mica flakes are relatively unmoved lends support to the hypothesis of A. N. Winchell (9) that the removal of graphite is mainly the result of a chemical process in which two interdependent reactions are possible: $C + 2H_2O \rightleftharpoons CO_2 + 2H_2$, and $C + CO_2 \rightleftharpoons 2CO$. The hydroxyl ion is necessarily present in both idocrase and tremolite and the presence of carbon dioxide is certain, for it was released in the formation of wollastonite from limestone. It is remarkable, however, that even where the silicate zone is negligible the limestone is still bleached and the graphite concentrated in an outer zone. Whilst it is possible that the carbon dioxide from silicated areas was swept along the veinlet, water vapour must be considered as the important factor in these reactions. Both reactions are displaced to the right by a rise in temperature and to the left by an increase in pressure. Under conditions of constant volume a temperature gradient would allow removal of carbon near the vein with deposition at a certain distance. Such conditions would be expected to produce a variation in grain-size frequency, especially an increase in the zone of deposition. In such a system with two possible gas phases, equilibrium can obtain over a wide range of temperatures, but, although the reactions under discussion are initiated at temperatures below $500^\circ C.$, that involving steam is of negligible *rate* below $550^\circ C.$, and that involving carbon dioxide is negligible below $600^\circ C.$; according to Taylor and Neville (10) the presence of calcium carbonate has only a slight catalytic effect. Even at temperatures $100^\circ C.$ higher the reactions are slow, and Winchell (9) considers that $700^\circ C.$ is a lower limit of appreciable transport of carbon. Higher pressures raise the temperature required to maintain a particular state of equilibrium, but the velocity of the reaction is probably not affected.

The grain-size frequency histograms of fig. 3 show features in accord with such a means of transport, especially as the suggested mechanism involves a surface reaction. The histogram on the right of fig. 3 represents the original size frequency of the graphite grains and shows an acute maximum in the small grain-sizes. The smaller the grain the greater is the surface area relative to the volume and, as the efficiency of solution or reaction is a function of area, the smaller the grain the more rapidly will it be removed. Thus the continued removal of graphite near the vein led to a relative decrease in the frequency of the smaller grain-sizes with a resultant increase in the mean diameter. Deposition of some part of the graphite on existing grains led to an increase in the frequency of the larger grain-sizes at the graphite culmination.

The skarn zones.—The formation of wollastonite, diopside, and tremolite as zones is very well demonstrated by the data expressed by fig. 5. It is admitted that a count of mineral grains cannot represent true concentrations by weight without a detailed knowledge of size frequencies; thus, for instance, the peak at 15 mm. in the diopside curve D is due to a decrease in grain-size. Nevertheless, the antipathy of this curve to that of tremolite and the curves of both these silicates to that of free quartz is clearly shown, demonstrating the separation of the mineral assemblages. This zoning of the silicates is coincident with a falling temperature gradient at a constant pressure, a factor which was clearly important in their formation. It has long been realized that, at a given pressure, metamorphism of magnesian limestones with excess silica proceeds in a regular sequence of steps with increasing temperature—Eskola (4) and Bowen (11). In the example described, a tremolite-diopside assemblage is first formed, then diopside, and finally a wollastonite-diopside assemblage separated by an idocrase sheath from a vein containing feldspar.

It is possible to formulate a number of equations for the formation of tremolite and diopside, for these minerals may arise from talc as a result of a chain of reactions or by direct reaction between dolomite and quartz. This may depend on the rapidity of establishment of a particular temperature of transformation. The following equations are suggested by Bowen (11) for the production of (a) tremolite from siliceous dolomite and (b) diopside from tremolite:

Low temperature.



High temperature.

The second reaction takes place at a higher temperature than the first.

Some of the diopside granules certainly exhibit a fibrous structure in the outer limits of the zone, which may be a residual feature, but it seems possible that the isotherms determining these reactions were rapidly established allowing formation of both silicates directly from the dolomitic portion of the limestone. Then, presumably, they gradually moved outward a distance equal to the width of the wollastonite zone, for we can assume that the quartz selvage containing calcite, quartz, and wollastonite represents a definite and constant temperature.

Near the vein illustrated by fig. 4 the diopside constitutes approximately 8% of the limestone and has evidently utilized the detrital quartz and the magnesia originally present in the form of 6% magnesium carbonate (table 1). The quartz content in the unaltered limestone near the vein does not exceed 2%, which thus implies that there was an addition of silica as well as the utilization of the original quartz. These remarks may also apply in the case of tremolite. Such a dual source of silica in skarns has been noted by Lindgren (12), although more generally the original quartz reacts less readily than the already ionized silica introduced from the magma. This introduction can be demonstrated clearly in microsections, for intergranular stringers of quartz bordered by diopside ramify far in advance of the wollastonite boundary. The silica may have been introduced as a solute in super-critical steam, this medium also removing graphite into an outer zone by the reactions discussed above.

The concentration of introduced silica should fall with increasing distance from the vein, for diffusion into the wall-rock depends on the temperature and pressure gradients which fall away from the intrusion. A zoned order of minerals may arise due to the resulting variation in the proportion of silica to magnesia, and it is significant that the minerals tremolite; diopside, and wollastonite are in order of decreasing dedolomitization. The formation of calc-silicate zones associated with a granitic apophysis at Port Shepstone, Natal, is attributed by Hatch and Rastall (13) to a diffusion mechanism with a fall in silica concentration away from the intrusion. Thus several interdependent factors, the temperature, pressure, and silica concentration gradients, are possibly concerned in the genesis of the mineral zones.

A volume for volume replacement of wollastonite for calcite and of idocrase and garnet for wollastonite is assumed. If the compositions are calculated from the optical properties, the comparison of the weights of ions in equal volumes of calc-silicate minerals and magnesia-poor limestone indicates that the calcium ion is not greatly involved in the substitutions. Some small exchange takes place during wollastonite

formation, but not in the replacement of wollastonite by idocrase and grossular, in which case it is the amount of silica per unit volume which decreases as a result of the substitution. This may account for the interstitial quartz with optical continuity which is associated with the grossular and idocrase. There was evidently a primary influx of silica which was in small part released in the form of quartz during the addition of alumina, magnesia, and iron to form grossular and idocrase in the larger veins.

The nature of the wollastonite formation is apparent from the quartz selvage containing calcite and wollastonite granules. In this simple reaction of silica with calcium carbonate the silica must have been continuously supplied from the intrusion and was probably transported through the enveloping skarn by super-critical steam, as suggested by the experiments of Gillingham (14), in which wollastonite was formed by reaction of steam-borne silica with Iceland-spar. The silica showed different rates of transfer to different 'collectors', indicating that a chemical potential is a possible factor in such a mechanism.

Fig. 4 shows without further discussion that the supply of silica is out of all proportion to the width of the intrusive. The quartz-felspar dikelet must have been continuously replenished, silica being rapidly absorbed by the limestone. In the early stages of the intrusion the material may have been more siliceous and, significantly, vein terminations are quartz-rich and are without appreciable skarn. When felspathic components entered the dikelet idocrase was formed by reaction with the early formed wollastonite. The small quartz-felspathic veins are almost certainly connected to the pegmatitic top of the main granite dike, and it is possible that the highly siliceous fluid originated from this pegmatitic phase. The vapour pressure created by the separation of such a phase may explain the degree of penetration of silica into the limestone wall-rock.

The main skarn vein may be the upward extension of a thinning pegmatite, for, as noted above, small granitic apophyses are seen to pass into skarn veins at a distance from the main intrusion.

The temperature of formation.—The well-known reaction expressing the formation of wollastonite can only be univariant in a closed system. Certainly the vapour pressure of the carbon dioxide would be reduced by dissipation in such metasomatic processes, with the result that the temperature of formation may be lowered to an unknown extent. This aspect is fully discussed by Eskola (4) and Bowen (11). The fact that bleaching occurs along structural planes in the western quarry of Lough

Anure and is common along bedding planes in many other granite-limestone areas indicates that the system may be relatively open. The association of calcite, quartz, and wollastonite reveals that there was a maximum temperature above which the quartz selvage was never raised; namely, the temperature at which the reaction $\text{CaCO}_3 + \text{SiO}_2 \rightleftharpoons \text{CaSiO}_3 + \text{CO}_2$ is in equilibrium at a certain pressure.

The temperature relations of the system $\text{CaO-SiO}_2\text{-CO}_2$ have been investigated in great detail by Kröger and Illner (15 A) at normal pressures. With silica in excess of calcium carbonate, the metasilicate reaction becomes stabilized at about 550°C ., but commences at much lower temperatures. In the experiments of Gillingham (14) wollastonite was formed at temperatures as low as 405°C . at a pressure of 248 atmospheres, but no attainment of equilibrium is claimed. Whilst it is possible for wollastonite to form at quite low temperatures, it would seem that the Goldschmidt pressure-temperature diagram as reproduced by Bowen (11) is a probable approximation and almost certainly an upper limit for reaction temperatures under conditions of equilibrium. At a pressure of one atmosphere an equilibrium reaction temperature not far below 500°C . is postulated, at an assumed pressure of 800 atmospheres (where the gradient of this P.T. curve becomes small and nearly parallel to the pressure abscissa) this temperature is near 750°C . and is the upper limit of the temperature of skarn formation. In the relatively open system of Lough Anure the temperature will be considerably lower, depending on the degree of escape of the carbon dioxide.

The reaction is, however, complicated by the presence of foreign substances (15 B). Whilst steam does not influence the reaction, halides increase the velocity and the presence of fluorine raises the temperature of stabilization. As idocrase accompanies wollastonite at Lough Anure fluorine was possibly present during the formation of the latter mineral.

As discussed above, 500°C . may be the minimum temperature for the transport of carbon, but even at temperatures 100°C . higher the reaction is slow and time is not unlimited when such minor intrusions are considered. Although it is not possible to be precise with regard to the actual temperature it was certainly well below 750°C ., and on the present hypothesis for carbon removal some temperature above 550°C . might be expected. The great width of the skarn envelope compared with that of the dikelet suggests that the temperature gradient from the vein cannot have been steep, and it is possible that the temperature of the whole sedimentary mass may have been raised by the approach of the later granite and intrusion of the larger dikes.

Summary.—A series of calc-silicate skarn veins is described; these occur in a limestone mass surrounded by granite in the Dalradian of western Donegal.

The skarn which borders these veins exhibits a zonal arrangement of the constituent minerals, idocrase and garnet, wollastonite, diopside and tremolite, which are enveloped by a zone of decolorized limestone. A central quartz-felspar dikelet is present in some cases.

The processes envisaged are the removal of graphite to an outer zone by means of a reversible reaction involving carbon dioxide or water; the addition of silica to yield wollastonite in an inner zone and diopside and tremolite in outer cooler zones, followed by an influx chiefly of alumina to produce idocrase and grossular by replacement of the wollastonite.

The sequence of zones is that of the established order of silicate formation with increasing temperature in a dolomite with excess quartz. The presence of wollastonite and calcite in equilibrium with quartz is taken to indicate a temperature lower than 750° C., and a temperature higher than 550° C. is probable for reactions involving the removal of graphite.

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