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Some zoned skarns from granite–marble contacts near Puyvalador, in the Quérigut area, eastern Pyrenees, and their petrogenesis.

(With Plate XIX.)

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Summary. Descriptions, with chemical and mineralogical data, are given of zoned wollastonite–grossular–clinozoisite skarns found at the contact of limestone and granite at Puyvalador, near Quérigut, France. It is shown that the silica and alumina necessary for the formation of the skarn were supplied by the adjacent granite, which in return received lime from the marble replaced by the skarn zones. The modified facies of the granite in contact with the skarn is also described; it shows evidence of migration of silica towards the contact and of accumulation of lime derived from the neighbouring marble.

Similar, but not identical, changes are found at other localities along the Quérigut granite contact with limestone. The features of the Puyvalador granite–limestone contacts are compared and contrasted with those described from some other regions. The contact rocks dealt with here are characterized by the presence of abundant clinozoisite, indicative of relatively low temperatures and abundance of water at the contact in the later stages of evolution of the granite.

THE zoned skarn rocks to be described below were collected from near the southern border of the granite massif of Quérigut–Millas, one of several acid intrusions probably of Carboniferous age cutting the lower and middle Palaeozoic rocks of the eastern Pyrenees.[1] The granite and the contact metamorphic effects induced by it in the surrounding

[1] The general geological structure of the eastern part of the Pyrenees has been briefly described by Raguin (1938) and Abrard (1948); a summary of recent views on the relationships between the main groups of older rocks in the central and eastern Pyrenees is given by de Sitter (1956).

beds were described by Lacroix, in two detailed and now classic memoirs (1898, 1900), which remain the best description of the rocks in the Quérigut area. In this work Lacroix gave a convincing demonstration of the importance of materials added to the sedimentary rocks from the granite magma during the period of metamorphism. The Quérigut area has thus been well known for many years as a result of Lacroix's descriptions of the felspathization of the schists bordering the intrusion, and of the appearance of new minerals, particularly garnet and epidote, in the limestones within the aureole of the granite. As his main conclusion, Lacroix affirmed that large-scale contamination of the granite by the calcareous and interbanded calcareous and siliceous contact rocks led to the production of hornblende-granite, which is observed along parts of the contact of the main intrusion with the calcareous or calcareo-siliceous rocks, and of more basic rocks (diorites, norites, hornblende-peridotites), small bodies of which are observed at several localities. This paper will deal only in passing with the genesis of these intermediate and basic rocks.

The Quérigut–Millas intrusion forms an elongate mass of granite, some 55 km. in length, lying between Ax-les-Thermes and Perpignan (see inset to fig. 1). The accompanying sketch-map (fig. 1), based mainly on the map given by Lacroix (1900), with additions from the detailed map of the French Geological Survey (Quillan Sheet, 1:80 000, 1938), shows the distribution of the main groups of rocks in the western part of the Quérigut–Millas intrusion. These have been fully described by Lacroix, and at present reference will be made only to the limestone and to the interbanded calcareous and siliceous rocks forming much of the enclosed belt of meta-sedimentary rocks near the southern border of the intrusion (the *zone enclavée* of Lacroix). The petrography of the granite and some of its modified facies are referred to in a later section of this paper.

Preliminary laboratory work early in 1954 was carried out on specimens brought from the Quérigut district several years previously by members of the Department of Mineralogy and Petrology, Cambridge University. Later, the writer had the opportunity of visiting the field and examining a number of the contacts. The main localities referred to in the following pages are indicated on the accompanying sketch-map (fig. 1).

The limestones and the calcareo-siliceous rocks: general description.

The unmetamorphosed limestone is a fine-grained, massive rock, light to dark grey in colour. Along the granite contact it is recrystallized,

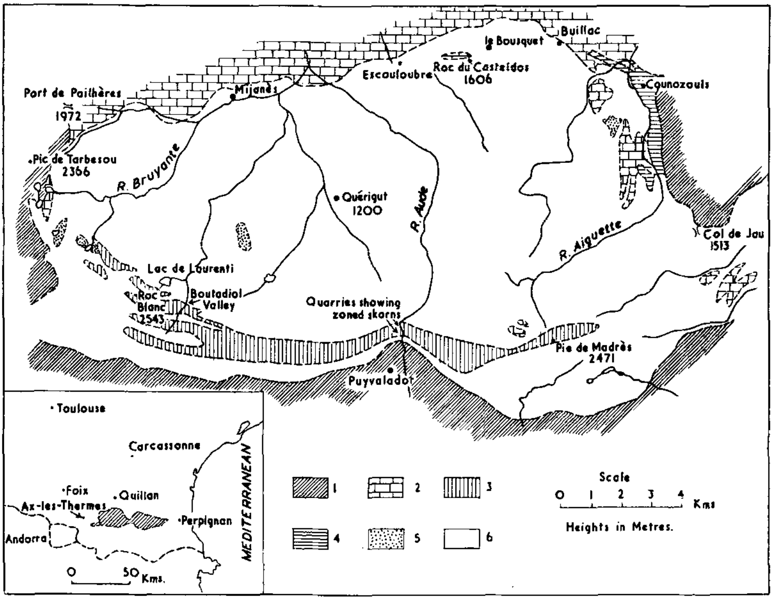

FIG. 1. Sketch-map of the western part of the Quérigut–Millas intrusion. 1. Lower Palaeozoic rocks, mainly argillaceous schists. 2. Middle Palaeozoic, mainly limestone. 3. Interbanded calcareous and siliceous rocks (Devonian). 4. Liassic sediments. 5. Intermediate to basic igneous rocks. 6. Granite, principally porphyritic biotite-granite, but including hornblende-granite near the boundary with calcareous rocks in many places on the southern part of the intrusion. (Inset map shows the general location of the Quérigut-Millas intrusion.)

usually with noticeable increase in grain-size, to a white or light yellowish marble. This is generally hard and compact, though occasionally weathered on the surface to a soft friable crust. In nearly every specimen examined it is composed very largely of calcite, but dolomite also occurs at a few localities. When the limestone comes into contact with the granite a skarn zone is sometimes developed, the skarns associated with dolomitic marble being distinct from those associated with the normal calcite marbles.

Metamorphism of the calcareous rocks interbedded with quartzitic or argillaceous bands has produced a variety of calc-silicate rocks (see Lacroix, 1898, pp. 16–17, 26–28, 39–40; 1900, pp. 7–9, 14–15). These are massive, hard, sometimes flinty rocks, often banded, and generally pinkish or greenish in colour. Their composition, dependent mainly on the relative amounts of limestone and silicate rocks in the original sediments, is very variable; nevertheless, the following four broad groups may be recognized: grossular-bearing marbles grading to coarse-grained green and pink calc-silicate rocks (including the *grenatites* and *épidotites* of Lacroix), which are sometimes imperfectly banded; calc-silicate rocks carrying potash felspar, which are reasonably common and are often encountered in the vicinity of granite and aplite veins, towards which latter there sometimes appears to be more or less perfect gradation; calc-silicate rocks carrying biotite, only a few of which were recorded; and hornfelses (with or without hornblende) made up essentially of diopside and plagioclase, which are often interbanded with the calc-silicate rocks of the first two groups noted above.

Occurrence and petrography of the zoned skarn rocks.

Zoned skarn rocks have been found at several localities in the Quérigut district where the granite, or veins of granite and aplite, are observed in contact with nearly pure carbonate rock; they may occur either in the limestone proper, or in limestone members of the banded calcareo-siliceous rocks. The finest specimens seen occur among the calcareo-siliceous rocks at a locality about $1\frac{1}{2}$ km. north of Puyvalador. The Puyvalador zoned skarns are found in quarries in the belt of calcareo-siliceous rocks at the point where it meets the Aude river. Fig. 2 shows a plan and sections of the quarries, which open on to a secondary road (D 32, leading from the main road [RN 118] to Quérigut). Here the belt of calcareo-siliceous rocks, bordered on both sides by biotite-rich granite, is exposed along the Aude valley between the road junction and a small stream that enters the river a little over 400 metres to the north. The road section (fig. 2, A and B) shows good exposures of banded calc-silicate rocks with several marble bands and layers of dark diopside–plagioclase hornfels. Veins of granitic rock (up to 3 or 4 metres in thickness) cut the meta-sedimentary rocks at several places, but the contacts are sometimes partly hidden by drift. The large quarry (quarry 2) near the north end of the section is cut into banded epidote- and garnet-rich calc-silicate hornfelses with ribs of marble, and these rocks are seen here in contact with thin veins of granite.

Section C (fig. 2) shows a sketch across the large, now disused quarry (quarry 1) at the road junction. The main rock exposed in it is an almost pure, white marble, which grades near the southern edge of the quarry, before the granite contact is reached, to a fine-grained grey marble with large porphyroblasts of garnet. Cutting the limestone are several small irregular masses of granite. These are up to 2 metres thick and often send out thin veins up to 5 cm. thick into the adjacent rock. The best zoned skarns are seen at the junction of the most southerly of these granite bodies, and its associated veins, with the limestone in the upper part of the quarry wall, and good specimens may be collected from the rubble which partly fills the quarry. No development of skarn was seen around the large granite vein in the central part of the quarry, but a thin

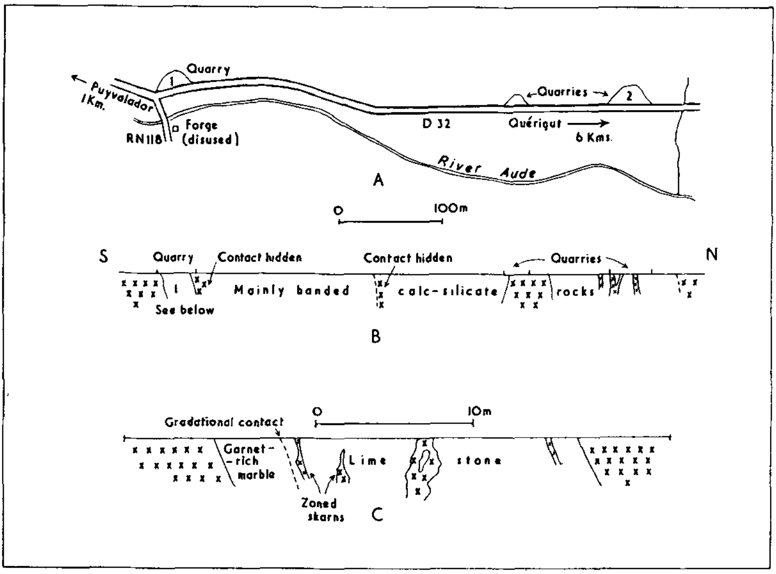

FIG. 2. Sketch-plan and sections of quarries near Puyvalador. A and B. Plan and section along road (D 32) where belt of interbanded calcareous and siliceous rocks meets the Aude valley. C. Section across large quarry (quarry 1) at road junction (RN 118–D 32).

aplite vein on the northern side shows a discontinuous layer of pinkish clinozoisite at its contact with the marble.

In the accompanying figures (3–5) are shown the arrangement and composition of zones in typical skarns collected from quarry 1 (fig. 2). Noteworthy in many of these rocks is the beautifully marked regularity of the separate zones, both in the exomorphic skarn and, to a lesser extent, in the adjacent modified granite. Next to the marble wollastonite forms an almost monomineralic zone, up to 4 cm. wide, and occurs in interlocking prisms usually aligned more or less at right angles to the contact with the marble. In section (pl. XIX, fig. 1) it is seen to carry numbers of tiny shapeless crystals of diopside, which may also form a very thin zone, observable in hand specimens as a distinct greenish line,

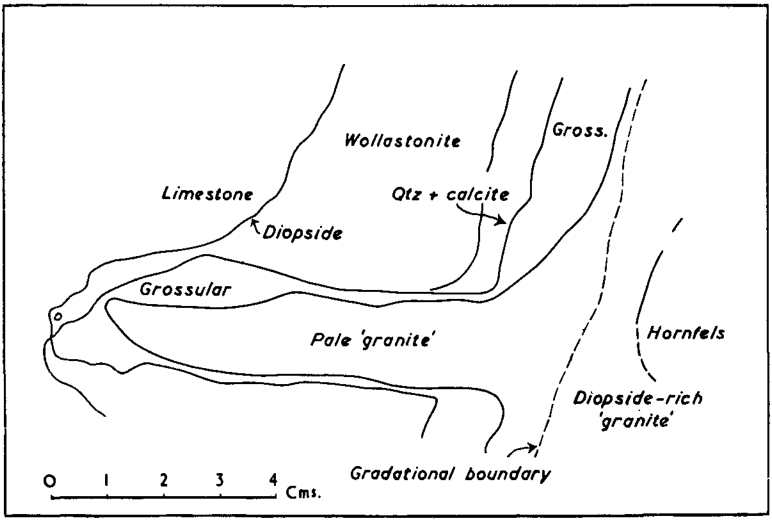

FIG. 3. Sketch of zoned skarn contact (61242), quarry at road junction north of Puyvalador, showing general arrangement of exomorphic skarn zones and modified 'granite' zones.

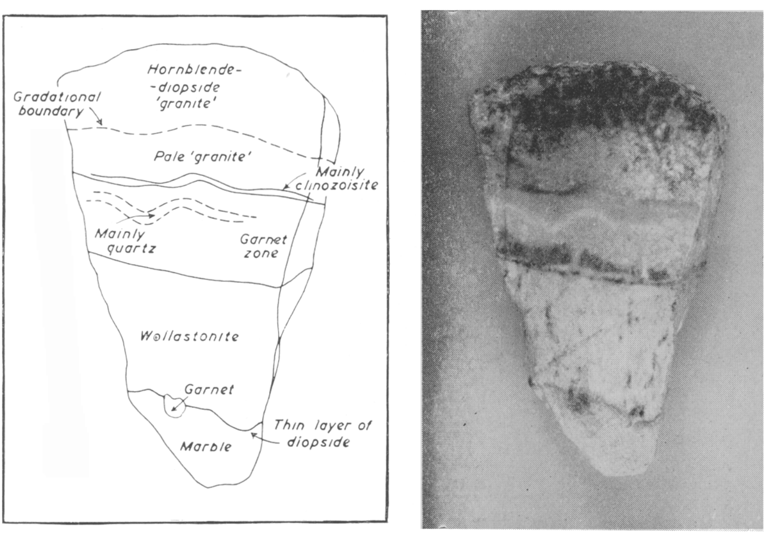

FIG. 4. Sketch and photograph of zoned contact from quarry at road junction north of Puyvalador. (Scale in centimetres.)

between the marble and the wollastonite. Other minerals in the wollastonite zone include grossular and idocrase (pl. XIX, fig. 1), crystals of which sometimes produce a brownish speckling on the surface of the zone (fig. 4).

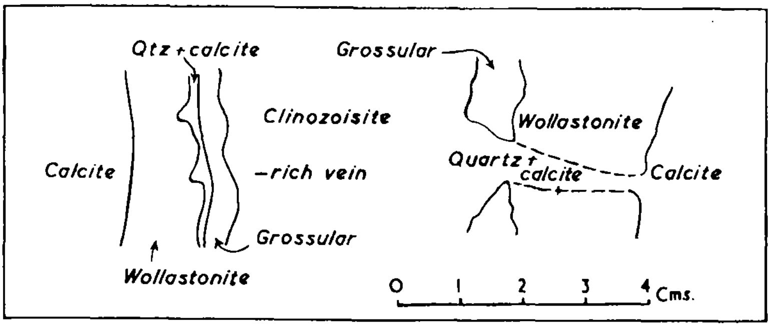

FIG. 5. Sketch showing clinozoisite-rich modified vein lined by exomorphic skarn zones, quarry at road junction north of Puyvalador.

In most specimens the wollastonite zone gives place abruptly to a pinkish-brown grossular zone, but occasionally a narrow layer in which quartz and calcite are predominant is seen between the two zones (figs. 3 and 5). Under the microscope this layer is seen to consist of a more or less equigranular mass of calcite and quartz, often unevenly distributed and usually accompanied by a little diopside. Occasionally the quartz

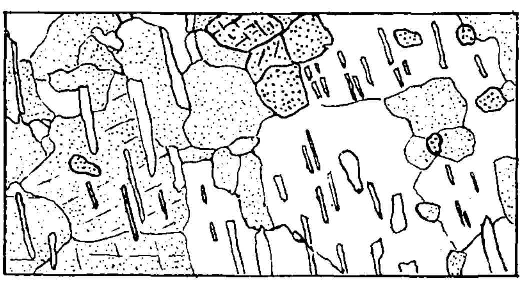

FIG. 6. Camera-lucida sketch of quartz-calcite zone between wollastonite and grossular zones (61483), showing little prismatic crystals of wollastonite within calcite and quartz. Note also small irregular grains of diopside. (Ordinary light, ×70.)

and calcite grains enclose little acicular wollastonite crystals, usually showing parallel orientation and optical continuity within the one host crystal (fig. 6).

The grossular zone is composed largely of an almost pure grossular, colourless in thin section (pl. XIX, fig. 2). It is often accompanied by a little idocrase; small, though variable, amounts of quartz, clinozoisite, diopside, and calcite may be present. Towards the outer part of the zone little irregular crystals of clinozoisite appear more constantly, and the rock grades rapidly to the modified granite. The arrangement and general nature of the modified granite zones are also indicated on the accompanying figures, and are described below (p. 718).

Here and there one or more zones may be missing, although the continuity of a zone is rarely interrupted for more than a few centimetres. Again, partial fracture of the exomorphic skarn zones by the adjacent granite is occasionally seen. Analyses of the wollastonite and grossular zones are given in table I (nos. 2 and 3).

TABLE I. Chemical data on Puyvalador contact rocks. Cols. 1–7: analyses of skarn and associated rocks. Cols. 8 and 9: figures showing gains (+) and losses (−), in grams per 100 c.c., in the marble during its replacement by the wollastonite and grossular zones.

	1.	2.	3.	4.	5.	6.	7.	8. $1 \rightarrow 2$.	9. $1 \rightarrow 3$.
SiO_2	4·50	49·41	49·07	73·66	57·55	70·00	61·40	+134·6	+147·7
Al_2O_3	1·58	2·12	16·78	13·87	15·56	15·14	16·36	+2·0	+50·4
Fe_2O_3	0·18	n.f.	1·58	0·32	0·81	0·74	1·91	—	+4·7
FeO	0·55	1·42	0·75	0·28	5·26	1·90	0·73	+2·7	+0·9
MgO	0·84	1·10	0·51	0·14	2·58	0·85	0·76	+1·0	−0·6
CaO	53·14	44·27	29·91	6·83	11·24	2·38	12·54	−13·0	−47·0
Na_2O	0·03	0·06	0·58	3·42	3·47	3·45	2·11	+0·1	+1·8
K_2O	0·02	0·03	0·11	0·84	2·43	4·56	2·03	+0·1	+0·3
H_2O-	0·02	0·02	n.p.	0·03	0·02	0·09	0·02	—	—
H_2O+	0·11	0·34	0·22	0·53	0·49	0·53	0·78	—	—
TiO_2	0·08	0·15	0·15	0·11	0·72	0·31	0·27	+0·2	+0·3
P_2O_5	0·06	0·06	0·02	0·01	0·19	0·11	0·15	—	—
CO_2	38·63	1·50	0·68	0·84	0·07	0·03	1·19	−101·7	−102·9
MnO	0·02	0·09	0·12	tr.	0·13	0·04	0·04	—	—
	99·76	100·57	100·48	100·88	100·52	100·13	100·29	—	—
Sp. gr.	2·72	2·97	3·26	—	—	—	—	—	—

1. Marble (61482), quarry at road junction, near Puyvalador (in this rock the figure for CaO includes 0·09 % SrO, determined spectrographically).
2. Wollastonite zone (61482), skarn in quarry at road junction, near Puyvalador.
3. Grossular zone (61482), skarn in quarry at road junction, near Puyvalador.
4. Pale modified 'granite' next to zoned skarn (61483), quarry at road junction, near Puyvalador.
5. Clinopyroxene-rich modified 'granite' next to zoned skarn (61482/83), quarry at road junction, near Puyvalador.
6. Biotite-granite (61529), Puyvalador area.
7. Clinozoisite-rich vein penetrating marble (61249), quarry near Puyvalador.

(Anal. W. A. Watters.)

Of the minerals in the skarns clinozoisite shows the greatest variation in quantity. In many specimens it is present only in a few small crystals at the boundary of the grossular zone and the modified granite. Sometimes, however, it forms a thin, almost monomineralic layer on the outer side of the garnet, and grades fairly rapidly to a pale-coloured clinozoisitized 'granite' (fig. 4). In a few specimens the marble is penetrated by thin veins, which are bordered by well-developed wollastonite and grossular zones and are found to consist almost entirely of clinozoisite and quartz (fig. 5).

Mineralogy of the skarn zones.

The properties of the more important skarn-forming minerals are given below:

Wollastonite is conspicuous in pearly white prisms up to 15 mm. long. In thin section the crystals have a tabular to prismatic habit; in all the sections examined, however, no definite crystal faces were recorded. The optical properties of the wollastonite (α 1·618, β 1·632, γ 1·635, $2V_{\alpha}$ 35°) and the chemical composition of the zone (table I, no. 2) indicate that it lies close to pure calcium silicate. Alteration products are usually rare. In a few places, e.g.[1] 61258, it may be almost completely replaced by finely divided calcite through which the original outline and cleavage traces of the wollastonite may still be seen. In other cases, e.g. 61478, the crystals are crossed by a network of thin veins of an undetermined pale to dark brown mineral in tiny flake-like grains showing medium birefringence. This may be similar to the decomposition product noted by Osborne (1931, p. 295) on wollastonite from Marulan, New South Wales.

Grossular. In hand specimen the grossular zone is light pink through pinkish brown to brown in colour; some of this variation is due to the presence of other minerals, particularly quartz (fig. 4). The garnet itself is mainly light pinkish brown, but there are occasional small areas of considerably darker colour (fig. 4). However, the optical properties of the mineral appear to be constant, and the cause of the colour variation is not yet understood. The mineral occurs in equidimensional crystals up to 5 mm. across; these are usually shapeless except at the boundary with interstitial quartz, towards which the garnet may show well-developed dodecahedral faces (pl. XIX, fig. 2). In thin section it is

[1] Numbers refer to catalogued specimens in the Harker Collection, Department of Mineralogy and Petrology, Cambridge.

almost colourless, and the refractive index, ranging between 1·740 and 1·745, suggests a composition close to pure grossular.[1]

The Puyvalador grossular is usually isotropic, but a few of the larger crystals show anomalous birefringence (0·001–0·002) and poorly developed sector twinning (61482); occasionally mainly isotropic crystals show small irregular birefringent areas. Minute dusty inclusions are frequent. Here and there a small amount of calcite penetrates the garnet crystals along thin cracks.

Grossular is a conspicuous member of skarns from other parts of the district, as well as in many of the calc-silicate hornfelses. In general its properties are close to those recorded for the Puyvalador mineral. A few rocks carry garnet relatively rich in andradite.

Epidote minerals. A mineral of the epidote group (normally clinozoisite) is a characteristic constituent of the Puyvalador skarns. Clinozoisite is a constant, though variable, mineral in the exomorphic zones, but is probably more conspicuous in some of the modified granites and aplites. However, its properties are fairly constant in all the rocks examined. In the few relatively iron-rich skarns seen the place of clinozoisite is taken by a strongly birefringent epidote.

The clinozoisite is usually pale green; rarely, pink-tinted crystals were seen. In section it is colourless, although the crystals always have a turbid appearance owing to large numbers of tiny inclusions. Both the low birefringence and the refractive indices (β = 1·716–1·726) indicate that the mineral is low in iron. Much of the clinozoisite shows irregular zoning under crossed nicols. A calculation of the composition of the clinozoisite in an analysed rock, the clinozoisite-rich vein illustrated in fig. 5 (61249; see table I, no. 7), showed that the mineral contains about 4·8 % Fe_2O_3, corresponding to a little under 10 mol. % of the $Ca_2Fe_3(SiO_4)_3(OH)$ molecule. The refractive indices for typical grains of this mineral are: α 1·714, β 1·717, γ 1·722.

Zoisite occasionally accompanies clinozoisite in the zone immediately outside the grossular. It is always subordinate to clinozoisite in the few sections (e.g. 61251/1, 61477, 61478) where it was recorded. It occurs in long prismatic crystals showing good (010) cleavage and parallel extinction. Its refractive index (β = 1·696) is appreciably lower than that of the associated clinozoisite.

[1] A preliminary attempt to determine the composition more accurately, by calculation from the analysis of the grossular zone (table I, no 3), indicated that the mineral is in fact close to pure grossular and contains about 5 mol. % of the andradite molecule.

Diopside is constantly present, though in small amount only, throughout the skarn zones, where it occurs usually as tiny irregular grains (normally less than 0·1 mm.) included by the other minerals (pl. XIX, fig. 1). Occasionally it may form aggregates of little crystals, generally between the wollastonite and grossular zones, but these are always local in extent. The diopside is colourless in section, and the refractive indices are: α 1·685, γ 1·716.

In a few localities a pale green hedenbergitic pyroxene (accompanying andraditic garnet) was recorded (see also Lacroix, 1900, pp. 9–11).

Prehnite is a very uncommon member of the skarn zones; where present it replaces in part the plagioclase of the modified granite next to the skarn (e.g. 61244/1, 61255/1, 61599), or fills thin veinlets penetrating the clinozoisite and grossular of the exomorphic zones.

Idocrase is a widely distributed constituent of the skarns, although it occurs in small amount only. In the wollastonite zone it is found in stout prismatic crystals, generally less than 1 mm. in length (pl. XIX, fig. 1). Within the grossular zone it forms shapeless crystals enclosed by the garnet. Sometimes a faint prismatic cleavage is visible, and there are often tiny opaque inclusions aligned parallel to the *c*-axis. Most of the crystals are a pale yellowish brown, although the colour may vary a little, even within a single grain. No pleochroism was seen. All the crystals examined are uniaxial negative, and the refractive indices vary from 1·716 to 1·722 for ϵ, and from 1·725 to 1·730 for ω, the higher values being recorded for the more distinctly brownish coloured crystals.

Most of the idocrase crystals show normal interference tints of the first order, sometimes patchily developed. A few specimens, e.g. 61245/4, show brownish-grey or greenish-brown tints, but only in very rare cases (61258) are anomalous Prussian blue colours seen. Occasionally the prisms show under crossed nicols a broad central core merging gradually towards the edge to a thin rim with slightly different interference tint. Rarely, as in 61257/5, a rough alternating concentric banding of the interference colours is seen.

Hornblende. Green hornblende forms a conspicuous member of a poorly zoned, dark-coloured skarn collected in quarry 2 from the contact between a granite vein and marble rich in garnet. It occurs in long prismatic crystals flattened parallel to (100), and is associated with abundant colourless epidote (β 1·732), calcite, pyrrhotine, and minor plagioclase and microcline.

Scapolite occurs rarely, being found only in a few specimens taken near the boundary between wollastonite and limestone (61393) and at a contact between limestone and a small veinlet of sheared aplitic granite (61484). It is found either as large prismatic crystals or in small irregular grains, which are often intergrown with quartz. The optical properties suggest compositions in the middle part of the mizzonite range.

Sulphide minerals. As noted above, a certain amount of pyrrhotine occurs in a hornblende-rich skarn from quarry 2. It forms irregular vein-like areas, bronze-yellow in colour, cutting the other minerals and often penetrating them along thin cracks. It is accompanied by a few silvery-white grains of arsenopyrite.

Genesis of the exomorphic skarn rocks.

It has been shown above that granite veins penetrating marble in the Puyvalador area are often lined by exomorphic zoned skarns, which have evidently been formed by metasomatic replacement of the invaded rock. If it is assumed that little or no change in the volume of the replaced rock has occurred, then it is possible, knowing the compositions and specific gravities of the marble and the adjacent skarn zones, to calculate the materials added to and lost by the marble during this transformation. This has been done for one of the Puyvalador rocks (61482), and the data are given in table I (cols. 8 and 9).

It is readily seen that the main addition to the marble in the formation of the skarn has been of silica and alumina. On the other hand some lime has been lost by the marble, and this has moved out into the neighbouring granite. It is probable that the small amounts of iron oxides, alkalis, titania, and manganous oxide present in the skarn have been introduced from the granite. On the other hand, the magnesia in the wollastonite and grossular zones has probably been derived from the breakdown of subsidiary magnesian carbonate in the limestone, the presence of which is also suggested by the common occurrence of accessory diopside in the marble. However, there has apparently been some movement of magnesium within the zones, shown not only by the loss of magnesia in the grossular zone but also by the frequent development of a thin layer of diopside crystals on the inner side of the wollastonite zone (pl. XIX, fig. 1).

The figures in table I show strikingly how silica has moved into the marble in advance of the alumina, leading to the beautifully marked and regular separation of the wollastonite and grossular zones that characterizes the Puyvalador skarns. Commonly the wollastonite zone has a considerably larger volume than the grossular (fig. 3), indicating a greater addition of silica to the limestone, relative to alumina, than is shown by the calculated figures, which refer to equal volumes of replaced marble for the two zones. However, the relative volumes of the zones may be quite variable, and the wollastonite zone itself is sometimes absent. This has been noted in particular at some other parts of the contact (e.g. in the Boutadiol valley, about 6 km. south-west of Quérigut; and near the Pic de Madrès, east of Puyvalador); the grossular zone is always present, however, and in the wollastonite-free rocks is more generally accompanied, on its outer side, by well-defined clinozoisite or clinozoisite-rich modified granite zones or by both.

The small wollastonite crystals that occur in the sporadic calcite–quartz layer (see fig. 6) indicate that some at least of the main wollastonite zone may have formed by the reaction of calcite and quartz. Experimental data on the equilibrium calcite + quartz $\rightleftharpoons$ wollastonite + carbon dioxide have recently been given by Harker and Tuttle (1956), who have discussed also the various factors that may modify in the field the simplified conditions for wollastonite formation obtaining in the laboratory. The difficulty of determining the conditions during growth of wollastonite in nature has also been referred to by Danielsson (1950) and Pitcher (1950). Despite this difficulty, an attempt is made here to assess the possible temperature of formation of the Puyvalador wollastonite, and at the same time to suggest an explanation of the occurrence of the zone of calcite and quartz between the wollastonite and the garnet in some rocks (e.g. 61242).

If the thickness of the Devonian and Carboniferous sediments lying above the Quérigut granite at the time of skarn formation was 1750–2000 metres,[1] then the pressure due to the overlying rocks at the border of the intrusion in this locality would have been about 500 atmospheres, corresponding to a temperature of 630° C. for the production of the wollastonite (Harker and Tuttle, 1956, fig. 5). This is probably a maximum value, since, if the carbon dioxide generated during the reaction is able to diffuse away, the temperature at which wollastonite first appears (for a given rock pressure) will be lowered (Danielsson, 1950, pp. 55, 67–68). Harker and Tuttle (1956, p. 249) consider that the pressure of CO_2 may generally be comparable with the rock pressure, although it may commonly be reduced, for example by escape of the gas through fissures. In the case of the present rocks it is probable that at some stage

[1] This estimate has been taken from a small-scale section (profile 49) given in a paper by Roussel on the stratigraphy of the Pyrenees (1905, pl. 1). The thickness given above, representing that of the rocks outcropping in the district at the present day, is used with some caution in the accompanying discussion.

at least the CO_2 was able to diffuse fairly readily through the marble, thus facilitating the formation of wollastonite. In some parts of the skarn, however, growth of a compact layer of wollastonite in interlocking crystals next to the marble probably hindered the escape of CO_2, the pressure of which gradually increased on the outer side of the zone, and inhibited the reaction of the calcite and silica. This gave rise to the observed calcite–quartz layer. The presence in it of tiny oriented crystals of wollastonite has already been referred to (see fig. 6), and it is probable that in parts of the zone at least the assemblage was very close to the four-phase equilibrium point for the temperature and pressure of CO_2 obtaining, and that escape of the CO_2 would have allowed the reaction to move readily to the right. However, as Harker and Tuttle point out (1956, p. 248), the effect of an additional component, in this case MgO, present in the diopside, on this equilibrium is still unknown.

There is little direct evidence regarding the order of growth of the different zones. Here and there, there are features suggesting that locally the wollastonite zone continued to grow after the formation of the major part of the garnet. For example, in 73445, a narrow tongue of fine-grained aplitic granite, continuous with the inner modified granite zone, breaks sharply through the garnet and penetrates the wollastonite zone, the thickness of which is increased around the tongue. Here the relations suggest that the narrow tongue acted as a channel through which silica continued to be introduced into the marble at a late stage in the formation of the skarn. Similar relations have been described by Pitcher for a skarn at Lough Anure, Co. Donegal, and he points out (1950, p. 138) that the supply of silica to the marble was obviously greater than could be obtained from the material of the vein itself, and that the latter must have been continuously replenished from below.

In other places, however (61483), although the pale granite has broken into both layers, sometimes penetrating as far as the marble, there is little or no thickening of the wollastonite zone, and the tongue is usually lined by a thin irregular layer of grossular. Thin sections (as well as close examination of hand specimens) show that these tongues are often highly charged with tiny grains of grossular, and the geometrical relations suggest that they have formed by intimate local penetration and replacement of the skarn zones.

The formation of grossular may be expressed by several alternative reactions, for example:

$$3CaCO_3 + Al_2O_3 + 3SiO_2 \rightleftharpoons Ca_3Al_2(SiO_4)_3 + 3CO_2,$$

or

$$3CaSiO_3 + Al_2O_3 \rightleftharpoons Ca_3Al_2(SiO_4)_3.$$

Such equations, however, may only be used in a very broad sense, as expressing the general relations between the components, and it is probable that the actual reactions were more complex, possibly involving intermediate compounds and being affected by the concentration of volatiles. Yoder (1950, pp. 232–6) attempted to synthesize grossular in dry sintering experiments on mixtures prepared in the stoichiometric proportions indicated above (as well as by possible reactions involving other constituents) but without success. He suggested, however, that grossular may form from intermediate compounds—some of which were prepared during the sintering experiments—which are presumed to be metastable.

It is probable that some at least of the grossular has formed by replacement of earlier formed wollastonite, and this is indicated by the growth of a thin zone of grossular around tongues of pale 'granite' cutting the wollastonite zone, referred to above (61483). No definite petrographic evidence of replacement of wollastonite by grossular has been found, however. One specimen (61252) shows a well-developed garnet-rich zone made up of isolated areas of grossular separated by wollastonite. Under the microscope the grossular crystals in this rock are seen to enclose occasional wollastonite prisms, but no textural evidence of active replacement of the wollastonite is observed.

On the other hand it is possible that the grossular has formed by a complex reaction between calcite, silica, and alumina. The co-existence of calcite and quartz in parts of the skarn has already been demonstrated, and the possibility remains that in places the grossular may have formed from an originally more widespread zone of calcite thoroughly impregnated with silica and alumina from the neighbouring granite. In such a case (for which there is as yet no direct evidence) growth of the two main zones would probably take place simultaneously, the formation of wollastonite and grossular being facilitated by the diffusion of the CO_2 produced by the reactions through the overlying rock.

Definite textural evidence of replacement of grossular by clinozoisite is also absent, but there can be little doubt that the formation of the sometimes abundant clinozoisite represents a gradation of the grossular zone outwards to an assemblage stable in contact with the modified granite (cf. Joplin, 1935). Within the modified granite zones much of the clinozoisite and zoisite seen is due mainly to the partial breakdown of plagioclase. Nearer the marble growth of clinozoisite has been favoured not only by lower temperatures prevailing in the later stages of formation of the skarn and probable accumulation of water at the contact, but also by the continued, though diminishing, influx of lime from the replaced marble into the marginal facies of the granite.

Description and genesis of the modified granite zones in contact with the skarn.

Against the outer side of the skarn zones at Puyvalador the granite of the veins shows a well-developed modified facies that is usually about 10–15 cm. in width, although it may be narrower. In many specimens this marginal facies is clearly divisible into two well-marked zones, an inner, light-coloured zone (next to the skarn), and an outer, darker zone which is usually the wider of the two. However, the volume of the pale zone is increased by the little tongues of pale 'granite' that penetrate the skarn zones in many places, and the volumes of the two zones are probably similar in many cases. Although the boundary between the zones is gradational, the transition from one to the other is usually over a short distance (< 5 mm.), and the contrast between them is nearly always distinct in hand specimen (fig. 3).

The normal granite of the Quèrigut intrusion has been described by Lacroix (1898, pp. 5–6) as made up essentially of potash felspar, oligoclase-andesine, quartz, and biotite. Preliminary modal analysis of several rocks from different parts of the intrusion shows that there is some variation in mineralogical composition, particularly in the relative proportions of plagioclase and potash felspar, and that some of these rocks should be classed as granodiorite or quartz-monzonite rather than true granite. However, insufficient is known of this variation to permit a detailed survey of the composition of the main mass.

A specimen of the granite (61529), from near the Puyvalador area, is described below, and the analysis is given in table I, no. 6. It is a coarse-grained rock, white in hand specimen, showing abundant large crystals of potash felspar, 2–3 cm. long, and little flakes of biotite. Apart from the large crystals the grain-size averages about 3 mm. Under the microscope plagioclase (making up about 30 % of the volume of the rock) is seen to occur in subidiomorphic tabular crystals often sprinkled with alteration products, chiefly sericite and zoisite. Most of the crystals examined lie between An_{36} and An_{28}; a few zoned grains (e.g. $An_{31 \rightarrow 20}$) are also present. The potash felspar, microcline microperthite (20 %), is mainly clear and unaltered and occurs in irregular plates carrying small inclusions of plagioclase and quartz. Cross-hatched twinning is constantly present, and most of the crystals show enclosed streaks of vein microperthite. Quartz (*ca.* 40 %) carries numerous tiny translucent inclusions and is always in irregular interstitial crystals showing strain shadows. Biotite (8 %) is the only ferromagnesian mineral present; it shows marked pleochroism from α light straw yellow to γ dark reddish brown. Here and there it is partially altered to pale greenish pennine. It contains numerous tiny semi-opaque needles (rutile ?), which often form a criss-cross pattern in basal sections. Accessory minerals are apatite, a little granular sphene, and zircon. A single crystal of muscovite was seen. In sections of the granite from some other parts of the intrusion the biotite is accompanied by a small amount of green hornblende, usually occurring in irregular clots associated with plagioclase (basic oligoclase or acid andesine).

As with some other parts of the intrusion near the contact with calcareous rocks the granite veins in the Puyvalador area often carry hornblende, but there is no direct evidence to show that this has formed because of the incorporation of calcareous material within the granite magma. In the contact areas examined from this and other parts of the district the characteristic change in the ferromagnesian minerals near the actual contact is the appearance of a colourless diopsidic augite. The presence of pyroxene near the contact is exemplified by the outer and darker zone of modified granite found in many of the veins at Puyvalador. The rock is medium-grained, and is made up essentially of microcline, acid andesine, interstitial quartz, and a colourless or very pale green diopsidic pyroxene, which, with the actinolitic amphibole forming the cores of some of the larger crystals, makes up to 20 % of the volume of the rock.

In typical specimens (61245, 61482) the approximate mode is as follows: plagioclase 30–40 %, microcline 25–30 %, quartz 5–8 %, and diopsidic pyroxene and amphibole 15–20 %. The texture shows considerable variation; sometimes the minerals are evenly distributed in small subidiomorphic crystals (0·50–0·75 mm.); in other cases the pyroxene tends to occur in clusters of prisms, or, with the plagioclase, is enclosed by large shapeless crystals of microcline (pl. XIX, fig. 3). From its texture and the relative amounts of plagioclase and potash felspar the rock is probably best termed a pyroxene-rich monzonite or quartz-monzonite.

The plagioclase lies within the sodic half of the andesine range, and on the whole is probably a little more calcic than the plagioclase of the normal granite of the intrusion. It occasionally shows slight irregular zoning, or it may be surrounded by a very thin rim of more sodic composition. The amount and distribution of alteration products of the plagioclase are rather variable. Most crystals show tiny inclusions of zoisite and sericite, but occasionally they contain relatively large shapeless grains of clinozoisite, and in one or two places the plagioclase is pseudomorphed by a fine-grained mass resembling saussurite. The microcline is usually perfectly fresh; it is only slightly microperthitic. Quartz is always in rather small interstitial crystals. The principal ferromagnesian mineral is an almost colourless pyroxene (β 1·698–1·700) forming squat subidiomorphic prisms that are often collected into irregular groups up to 5 mm. across. In many cases the pyroxene is mantled around an irregular core made up of interlocking crystals of a pale green to almost colourless actinolitic amphibole (β 1·651) (pl. XIX, fig. 3), and there is little doubt from the texture that the pyroxene has developed later than the amphibole. There are a few scattered flakes of biotite. Both the mica and the amphibole show numerous little included granules of sphene, which may also form large idiomorphic crystals or rims around iron ore grains. Accessory minerals are iron ore, apatite, and rarely zircon.

Towards the inner part of the above zone the dark minerals decrease in amount, and with the more widespread appearance of decomposition products of the plagioclase, and increase in quartz, the rock grades rapidly into the pale zone. This is formed essentially of plagioclase (45–55 %) and quartz (35–45 %) (pl. XIX, fig. 4). The plagioclase always carries numerous small grains of zoisite and less commonly sericite. Potash felspar (< 10 %) varies somewhat in amount in different parts of the zone. On the side against the skarn zones shapeless crystals of clinozoisite usually appear, and, as noted earlier, these may be abundant enough to form a thin, almost monomineralic layer against the grossular. If this zone is absent the pale 'granite' sometimes carries a few small grains of garnet at the margin of the grossular zone. On the other side small prisms of diopside begin to appear as the contact with the pyroxene-rich modified zone is approached.

The plagioclase of the pale 'granite' zone ranges between An_3 and An_{10}. The zoisite it contains is in the form of numerous tiny prisms or rod-like crystals with straight extinction, but in many places small irregular grains or clusters of grains showing properties typical of clinozoisite occur. The potash felspar forms small interstitial crystals or occurs as a thin rim around some of the plagioclase grains. The quartz is always in irregular crystals with numerous tiny semi-opaque inclusions (pl. XIX, fig. 4).

The analyses of typical specimens of these zones are given in table I, nos. 4 and 5.

It is difficult to determine the possible amounts of the constituents given up by the granite veins to the adjacent marble in the formation of the skarns, since no reliable analysis of an unaltered vein is available, and, in some cases at least, the veins differ somewhat in mineralogical composition from the adjacent granite of the intrusion. Even with analytical data it may be very difficult to compare the original unmodified rock with the modified facies, when the latter often shows a differentiation into two well-marked zones.

In the veins examined there often appears to have been a pronounced migration of silica towards the boundary with the skarn. This is brought out by the petrography of the modified granite and the enrichment of the pale 'granite' zone in quartz, and is strikingly shown by comparing the analyses of the two zones (table I, nos. 4 and 5). That silica continued to migrate into the marble up to a late stage in the formation of the skarn was suggested above. In one or two specimens the reaction between the marble and the granite has possibly been modified by interchange of material between the granite zones and a fine-grained plagioclase–diopside–biotite hornfels, small amounts of which are seen on the outer side of the pyroxene-rich modified zone (fig. 3). Some lime and magnesia may have been gained by the modified granite from this source; however, the hornfels is sharply bounded against the pyroxene-rich zone, and there is no apparent sign of interchange between the two rocks.

The migration of alumina from the modified granite to the marble is less easy to detect; the main mineralogical change reflecting the loss of alumina in the marginal granite is the crystallization of a pale diopsidic augite rather than hornblende. Migration of alumina towards the skarn contact probably also aided the crystallization of clinozoisite there in many rocks.

It was shown above that lime had been lost by the replaced marble, and the petrography and chemical composition of the modified zones show that some of this at least has been taken up by the granite. The lime shows a marked concentration in the monzonite zone (see table I, no. 5), and it is obvious that the main movement of lime within the modified granite has been opposed to that of silica. The gain in lime of the modified granite is attested by the following mineralogical changes: the appearance of pyroxene, often seen to be mantled around amphibole (pl. XIX, fig. 3); the gradual increase of clinozoisite towards the skarn zones; and the appearance of abundant accessory sphene developing at the expense of biotite, hornblende, and iron ore.

In some rocks the gradual increase in the amount of clinozoisite may be followed stage by stage to a final product formed essentially of clinozoisite and quartz. Excellent examples of such rocks are found in thin veins penetrating the marble (e.g. 61249; see fig. 5). Although these are lined by thin exomorphic skarn zones the mineralogy of the rocks (which may contain up to 55 % clinozoisite) and the chemical analysis of a typical specimen (table I, no. 7) suggest that more lime has been taken up by the vein than would be available from the marble replaced by the skarn lining the veins. It is possible, therefore, that these veins have formed channels into which some of the lime lost at other parts of the contact has been concentrated.

Other localities along the contact zone (e.g. Boutadiol valley, Pic de Madrès) often show hornblende-granite at the limestone boundary. In general the same mineralogical changes as recorded in the Puyvalador contacts are seen in these rocks. The appearance of a thin diopside-bearing granite zone between the skarn and the hornblende-granite is sometimes very conspicuous (e.g. 61376). However, marked differentiation of the marginal facies is seldom seen away from the Puyvalador locality, although clinozoisite may often form a definite layer against the grossular.

Comparison of the Puyvalador contact rocks with those of other areas.

Skarn assemblages analogous to those of Puyvalador have been described from many localities, e.g. Marulan, New South Wales (Osborne, 1931), Ben Bullen, New South Wales (Joplin, 1935), Barnavave, Ireland (Nockolds, 1937, 1950), and Ballachulish (Muir, 1953). However, these localities rarely show the often perfect skarn zonation characteristic of the Puyvalador rocks. In this respect the latter may be compared with the zoned skarns described by Tilley (1948, 1949, 1951) from the contact of Cambrian dolomites with the Beinn an Dubhaich granite in Skye. The Puyvalador skarns are comparable with some of the primary skarns of this area, but the development of ore skarns on the limestone side of the primary skarns is generally absent in the Quérigut area. Tilley (1949) has shown that at two localities in Skye (Kilchrist and Camas Malag) the grossular–wollastonite type of skarn found there has gained lime, which has migrated outwards from the dolomitic limestone; at the same time the magnesia eliminated from the skarn has moved inwards beyond the diopside zones of the skarn. In the Quérigut contacts, however, there is evidence of marked reciprocal reaction between the marble, which is non-dolomitic, and the granite, and the effects of the addition of lime to the marginal granite are particularly well shown. Analogous effects of reciprocal reaction are also seen at the other localities mentioned above.

At the Skye localities the effects of the essentially one-way transfer of material, especially alumina, from the granite to the dolomitic limestone, are expressed in the development of a marginal alkaline granite facies rich in potash felspar and containing alkali-bearing clinopyroxene and a little arfvedsonite. The marginal granite, however, is not noticeably desilicated, despite the transfer of silica to the adjacent skarn, and it is probable, as suggested by Nockolds (1950, p. 23), that such desilication only becomes apparent when the granite occurs as apophyses in the limestone. This is also suggested by different occurrences in the Quérigut district: at Puyvalador the modified granitic rocks showing marked desilication occur near the edges of veins penetrating the marble, and veins with quartz in only accessory amounts (e.g. 61388) are seen in the limestone in the Laurenti area, one km. south of the lake (fig. 1). At other parts of the contact (e.g. Boutadiol valley, Pic de Madrès), where a much larger mass of granite is against the marble, the marginal granite shows little or no desilication.

The alkaline modified granites that appear at the contacts in Skye, Barnavave, and Ballachulish show a marked enrichment in potash felspar relative to the normal granite. This has not been recorded definitely for the Puyvalador rocks. Nevertheless, in the Laurenti area veins (e.g. 61373, 61388, 61391) cutting the marble between $\frac{3}{4}$ and 1 km.

south of the lake show a high content of microcline, and although these rocks have not been studied in detail it is probable that they are analogous to the potash-rich rocks from Ballachulish, Barnavave, and Skye. These three localities resemble Puyvalador in the appearance of clinopyroxene in the modified facies. The pyroxene from the Skye and Barnavave rocks is alkali-bearing, but at Ballachulish no excess of soda over alumina in the marginal granite is found, and the pyroxene is a normal non-alkaline type. The only effect possibly attributable to the accumulation of a small quantity of soda-rich material in the final stages of consolidation of the monzonitic facies at Puyvalador is the presence of a few little wisps of a blue-green amphibole at the edges of some of the pyroxene crystals.

In the second main variety of primary contact skarns at Skye, namely the hedenbergite–plagioclase skarn, the associated granite shows evidence of incorporation of lime and is enriched in plagioclase. At Puyvalador the influx of lime into the granite has not resulted in an increase in the plagioclase content, owing apparently to the simultaneous migration of alumina to the skarn, and much of the lime gained has been taken up in the formation of pyroxene.

Summary and conclusions.

The probable sequence of events in the aureole of the Quérigut granite at Puyvalador may be briefly described as follows:

Contact metamorphism of the limestones and interbedded calcareous and siliceous rocks during the intrusion of the granite was followed by metasomatic replacement of the marble at many parts of the granite contact, with the production of skarns, up to 10 cm. wide and often zoned. From the temperature of formation of the wollastonite (above, p. 715) this has taken place under pneumatolytic conditions, and has involved the interchange of silica, alumina, and lime between the granite and the replaced marble. Finally, accumulation of volatiles in the crystallizing modified granite facies adjacent to the skarn facilitated the formation of abundant clinozoisite, the presence of which is a characteristic of the Puyvalador skarn contact rocks. Minor mineralogical changes connected with the final stages of contact activity were the production of very small amounts of prehnite in the modified granite, and the introduction of iron-rich solutions into the skarn at one or two places, leading to the formation of iron ores (magnetite and pyrrhotine) cutting the earlier minerals (see also Lacroix, 1900, pp. 9–11).

The very regular and often unbroken zonation of the skarns points strongly to a completion of movement in the greater part of the underlying granite during the period of formation of the skarn rocks and the modified granite zones. However, the presence of occasional fracturing of the skarn indicates that local minor movements in the magma continued to a late stage in the evolution of the contact rocks. It is not known to what extent this fracturing of the skarn may have further modified the composition of the adjoining granite.

In none of the contact rocks studied and described above has evidence been found of the production of hornblende-rich basic rocks, as was suggested by Lacroix (1898, 1900) for some parts of the contact in the Quérigut area. The features described show that the marginal facies of the granite in contact with the marble is developed on a small scale only, and shows the formation of pyroxene rather than hornblende.

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EXPLANATION OF PLATE XIX.

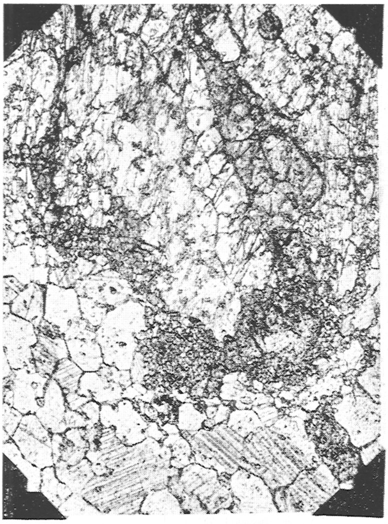
Puyvalador skarns and associated modified granite facies.

FIG. 1. Boundary between marble and wollastonite zone (61482). Note tiny included crystals of diopside, which also forms a very thin layer along the edge of the marble. The wollastonite zone shows a large prismatic crystal of idocrase. (Ordinary light, × 13.)

FIG. 2. Grossular zone, showing subsidiary quartz (61482). Note occasional dodecahedral faces developed where the grossular is in contact with quartz. The zone often shows crystals of diopside, clinozoisite, and calcite (not seen in the photograph). (Ordinary light, × 13.)

FIG. 3. Pyroxene-rich modified 'granite' facies (61482). Note prismatic crystals of plagioclase and pyroxene enclosed by microcline. The core of the large pyroxene crystal is formed of interlocking prisms of very pale green actinolitic amphibole. Other minerals are quartz and biotite (not seen in the photograph) and sphene. (Crossed nicols, × 13.)

FIG. 4. Pale 'granite' zone (61242). Mainly quartz and acid plagioclase (albite to albite–oligoclase), which nearly always contains numerous little rods and prisms of zoisite. The rock may contain an appreciable, but variable, amount of potash felspar. (Ordinary light, × 13.)



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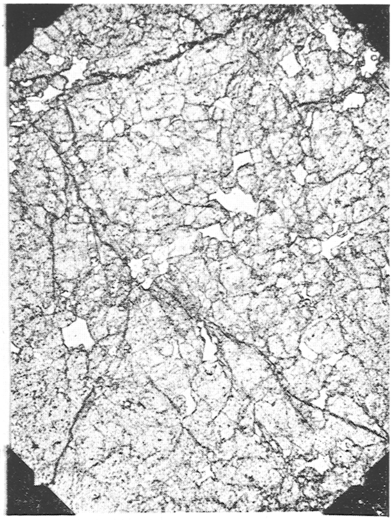

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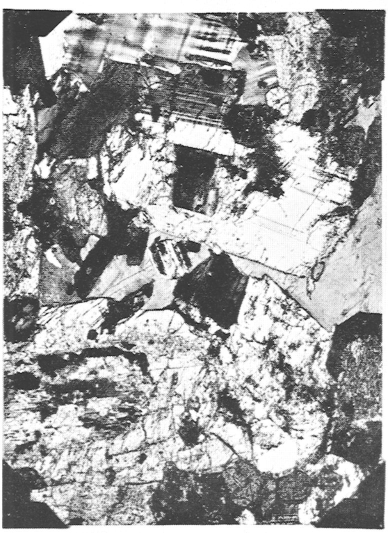

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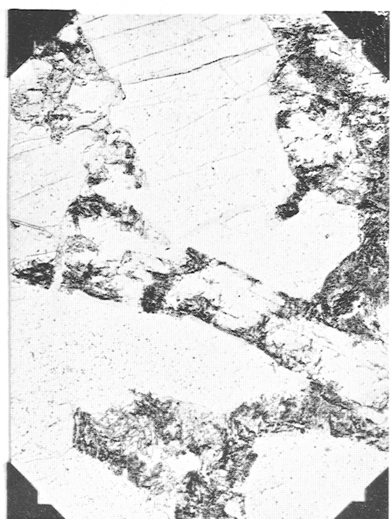

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W. A. WATTERS: ZONED SKARNS FROM THE PYRENEES