Polythermal metamorphism of limestones at Kilchoan, Ardnamurchan

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Summary. Jurassic limestones occurring in a screen between two ring dykes are shown to have undergone two periods of thermal metamorphism; the first characterized by a high ratio of $CO_2:H_2O$ and the second by a high ratio of $H_2O:CO_2$ in the vapour phase. The first metamorphism produced minerals characteristic of Bowen's decarbonation series. Some of these minerals became unstable in the second metamorphism and (OH, F) bearing minerals were produced. A stage of fracture-controlled replacement veins with mineral assemblages which indicate a varying $CO_2:H_2O$ ratio in the vapour and a general falling temperature sequence terminate the metamorphic history. Three new minerals, rustumite[1] ($Ca_3Si_2O_7.Ca(OH)_2$), dellaite[1] ($Ca_{12}Si_6O_{22}(OH)_4$), and kilchoanite ($Ca_3Si_2O_7$), of which the last has previously been described, are characteristic of the second episode of metamorphism.

Introduction

THREE-QUARTERS of a mile north of the hotel at Kilchoan an outcrop of Jurassic limestones occurs between the porphyritic dolerite intrusion of Glas Bheinn and a ring dyke of quartz gabbro. The former intrusion belongs to Centre One and the latter to Centre Three (Richey and Thomas, 1930).

The exposures are isolated and poor, and no contacts with the above igneous rocks are to be seen. Nor do exposures of the adjacent igneous rocks show any evidence of limestone contamination.

Both high and low grade assemblages can be found in the metamorphosed limestones, the latter more in the western outcrops. At the eastern end among rocks which are dominantly spurrite marbles and grossular-wollastonite rocks some exceptionally complex mineral assemblages occur. It is with these that the present paper is concerned as it is thought that they show evidence of repeated thermal metamorphism.

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[1] Dellaite has been named after Della M. Roy who synthesized and characterized this compound in the course of extensive work on the system $CaO-SiO_2-H_2O$. Rustumite is named after Rustum Roy who is well known for his work on synthetic mineral systems.

The mineralogy of the decarbonated and hydrated rocks

Bands of rock, up to six inches thick, which were originally nodular or concretionary limestones, show a complex series of mineral assemblages essentially reflecting variations in the initial composition of the sediment. The following mineral assemblages have been observed in a general sequence from one side of a rock band to the other; their boundaries are complex and irregular even within the limits of one thin section.

Calcite–Spurrite
Åkermanite–Merwinite–Monticellite
Åkermanite–Merwinite–Larnite–Spurrite
Åkermanite–*Merwinite–Larnite*–Rustumite–Spurrite } ± cuspidine
Åkermanite–*Rankinite*–Kilchoanite–Rustumite–Spurrite } grossular
Grossular–Merwinite–Larnite–*Spurrite*–Kilchoanite }
Grossular–*Spurrite*–Kilchoanite } ± idocrase
Grossular–Kilchoanite–Wollastonite }
Grossular–Wollastonite }

Those minerals which are in italics may be unstable as they may appear as isolated residuals, sometimes in optical continuity, set in the host mineral which follows them in the assemblage list.

Åkermanite occurs in colourless or faintly brown crystals with ω 1·647, ϵ 1·648 corresponding to $\mathrm{Ak_{65}Ge_{35}}$ in composition. In assemblages carrying rustumite it may break down to a very fine-grained aggregate of wollastonite, monticellite, and grossular in which these minerals are only identifiable on diffractometer traces. Where kilchoanite is present the pseudomorphs after melilite are much more diffuse, the grain size is slightly coarser and grossular, wollastonite, and idocrase are the only minerals which can be identified optically or on diffractometer traces.

Merwinite is similar to that occurring at Scawt Hill or Camphouse (Ardnamurchan). It may be replaced by colourless lamellae of an unidentified mineral in a regular pseudo-hexagonal array. It has not been possible to isolate this mineral for X-ray characterization but preliminary determination of Ca, Mg, and Si by means of the electron-probe gave values close to that of the host merwinite. The following optical properties were determined: α 1·630, γ 1·650±0·003, $(-)2V \pm 70°$, $\gamma \wedge$ twin plane $= 40°$, lamellae with simple twins parallel to their length were usually parallel to (100) of the host merwinite.

Rustumite, $\mathrm{Ca_3Si_2O_7(OH)_2}$. This mineral occurs in a zone between spurrite dominant and kilchoanite dominant assemblages as crudely tabular crystals up to 2 mm in length. It may carry many inclusions of spurrite, melilite or its alteration products, merwinite, larnite, and occasionally rankinite or kilchoanite.

Crystals are more or less equant with a tendency to be tabular on (100) and are colourless with a faint hazy turbidity. The cleavage is (100) poor, (010) and (001) very poor and lamellar twinning on (100) is common. The density is 2·86 calculated from the refractive indices according to the method described by Howison and Taylor (1957). The optical properties are α 1·640, γ 1·651, $-2V$ 80°, $\beta = b$, $\alpha \wedge c = 4$–6°.

As it was not possible to separate enough pure material for chemical analysis, the composition was determined by means of the electron-probe on material in a polished thin section, using pure wollastonite as a standard.

	Rustumite	$Ca_3Si_2O_7Ca(OH)_2$
SiO_2	33·8 ± 1 %	33·14 %
CaO	61·6 ± 1 %	61·89 %
H_2O	4·6 by difference	4·97 %

Electron-probe measurement showed that rustumite contained less than 0·2 % Fe_2O_3,Al_2O_3,MgO and microchemical tests showed it to be free of CO_2.

The following cell constants were determined from a single crystal extracted from a thin section:

a 7·62 Å, b 18·55 Å, c 15·51 Å (all ± 0·05 Å)
β 104° 20′ ± 10′, space-group Cc or $C2/c$, $Z = 10$
Twin axis [001]

X-ray powder data were also obtained from a concentrate and are given below:

d (in Å)	I	d (in Å)	I	d (in Å)	I	d (in Å)	I
6·90	w	2·52	ms	1·661	m	1·191	vvw
5·91	vw	2·37	w	1·613	m	1·168	vvw
5·46	vw(i)	2·29	m	1·548	vvw	1·151	vvw
4·60	w	2·20	vw	1·515	vvw	1·131	vvw
4·36	w(i ?)	2·16	vvw	1·465	vvw	1·116	vvw
3·76	w	2·10	vvw	1·433	vvw	1·085	vvw
3·19	s_3	2·03	vvw	1·404	vvw	1·044	vvw
3·10	w(i)	1·968	vvw	1·378	vvw	0·966	vvw
3·03	s_1	1·907	ms	1·350	vvw	0·954	vvw
2·89	s_2	1·855	vvw	1·321	vvw		
2·75	m	1·752	ms	1·260	vvw		
2·63	m	1·698	vvw	1·122	vvw		

(i) = impurity

With the large monoclinic cell it is difficult to correlate observed and calculated line-spacings for values of less than about 2·0 Å. For larger spacings most of those observed can be fitted with the calculated line positions, though there are a few lines which must be ascribed to impurity. The most likely impurities are spurrite, kilchoanite, or melilite, but the impurity lines do not correspond with the strong maxima of any of these minerals, so the nature of the contamination is unresolved. Consequent on the size of the unit cell, there is so much ambiguity in indexing the lines that it is not considered worth while giving (*hkl*) values with the *d*-spacings.

The appearance of rustumite is similar to cuspidine in thin section, though where the two occur together the higher refractive index of the former is apparent. The composition too is that of the hydroxyl equivalent of cuspidine. However, Van Valkenberg and Rynders (1958) have shown that substitution of F by OH is limited in cuspidine and further only the *a* cell dimensions show any correspondence.

A closer relationship is seen with tilleyite whose structure was determined by Smith *et al.* (1960) and which has the following cell dimensions: *a* 15·03 Å, *b* 10·27 Å, *c* 7·63 Å, *β* 105° 50′, the *a* and *c* cell dimensions of tilleyite corresponding to the *c* and *a* cell dimensions of rustumite. This suggests that rustumite is related to tilleyite by substitution of $Ca(OH)_2$ groups for $CaCO_3$ groups.

No evidence has been observed suggesting that rustumite develops at the expense of tilleyite, nor, as might be expected, has any parallel growth between the two been seen. At Camphouse (Agrell and Gay, 1961) and Kilchoan both minerals belong to the same stage of metamorphism. At the former locality when kilchoanite is developed tilleyite forms at the expense of spurrite, at the latter when kilchoanite is developed rustumite crystallizes along with spurrite.

The only minerals which occur as resorbed crystals in rustumite are larnite and occasionally merwinite, which suggests that the following reaction takes place:

$$2Ca_2SiO_4+H_2O \rightarrow Ca_3Si_2O_7Ca(OH)_2$$

If however silica metasomatism accompanied the introduction of water, other minerals than larnite and merwinite may have been out of equilibrium and contributed to the formation of rustumite.

Rankinite is occasionally preserved as drop-like crystals included in rustumite or spurrite. At Camphouse rankinite is seen partially replaced by kilchoanite but at the present locality the process of replacement is not seen. Its previous presence in kilchoanite rich assemblages is suggested by the latter's position between larnite-merwinite rich and wollastonite rich assemblages.

Kilchoanite, $Ca_3Si_2O_7$. The properties and occurrence of this mineral, which corresponds to phase *Z* of Roy (1958), have been described by Agrell and Gay (1961). It occurs here as coarse (1–2 mm) irregular interlocking crystals with no regular cleavage, recognizable by their dusty appearance and abnormal interference colours. It has the following optical properties: α 1·647, γ 1·650, $-2V$ 60°, dispersion marked $\rho > v$.

Inclusions of spurrite and diffuse pseudomorphs of grossular and idocrase ± wollastonite after melilite are common, inclusions of larnite and merwinite are rare. The spurrite sometimes occurs in small rounded crystals, groups of which may be in optical continuity, suggestive of replacement residuals. If this is the case kilchoanite could arise not only by the inversion of rankinite but the breakdown of spurrite. This implies that the vapour phase carried silica and that although spurrite and kilchoanite could be in equilibrium with each other, the spurrite was out of equilibrium with the vapour phase:

$$3(2Ca_2SiO_4.CaCO_3)+4SiO_2 \rightarrow 5Ca_3Si_2O_7+3CO_2$$[1]

Cuspidine occurs sporadically as clear inclusion free crystals of both idioblastic and xenoblastic habit. It is essentially restricted to rustumite-bearing assemblages. Its presence, like that of idocrase, is indicative of a small amount of fluorine in the vapour in the stage of metamorphism in which it was developed.

Wollastonite occurs in tough rocks with subordinate grossular replaced by idocrase separating the kilchoanite rich bands from calcite-spurrite marble. The wollastonite occurs in crystals of two grain sizes: porphyroblasts about 1 cm in length are set in a granoblastic matrix of crystals about 0·1 mm in length.

From the above relations one may infer that an earlier series of mineral assemblages was developed and that a later one associated with the development of (OH,F) bearing minerals was superimposed on it.

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[1] It could be argued that the resorption of spurrite is illusory. Thus at Camphouse it is common to see poikiloblastic spurrite crystals crowded with drop-like crystals of rankinite. If the inversion of rankinite to kilchoanite took place in the spurrite stability field the host inclusion relationship might be reversed during recrystallization.

The initial decarbonation assemblages were:

Spurrite–Calcite
Åkermanite–Merwinite–Monticellite
Åkermanite–Merwinite–Larnite–Spurrite
Åkermanite–Larnite–Spurrite
Åkermanite–Rankinite–Spurrite
Åkermanite–Rankinite–Wollastonite
Grossular–Wollastonite

The superimposed assemblages were:

$$\left.\begin{array}{l}\text{Spurrite–Rustumite–Grossular}\\ \text{Spurrite–Kilchoanite–Grossular–Idocrase}\\ \text{Kilchoanite–Wollastonite–Grossular–Idocrase}\\ \text{`Porphyroblastic' wollastonite–Grossular–Idocrase}\end{array}\right\}\begin{array}{l}\pm\text{cuspidine,}\\ \pm\text{alteration}\\ \quad\text{products of}\\ \quad\text{melilite}\end{array}$$

Mineralogy of late stage veins

The latest changes visible in these rocks are narrow (0·1–2·0 mm) discontinuous fissure and replacement veins. Some of these can be observed cutting all assemblages, but they are most noticeable in the kilchoanite rich portions of the rocks. The principal vein assemblages and the host mineral from which they were primarily derived are listed in table I.

These veins with their variable mineralogy show that at a late stage the rocks were intermittently fractured and affected by a vapour phase of varying CO_2, H_2O, CaO, and SiO_2 content. It is not possible, from the mutual intersections of the veins, to give in detail the order in which they were developed, but a general sequence with falling temperature is apparent. Local reversals occur, which may reflect variations in temperature, total pressure and ratio of $H_2O:CO_2$ in vapour phase. Probably the last two are the most significant as it is difficult to visualize sudden temperature fluctuations in a relatively large mass of rock being associated with such minute features as these veins.

Dellaite, $Ca_{12}Si_6O_{22}(OH)_4$. This mineral is similar to phase *Y* ($6CaO.3SiO_2.H_2O$) synthesized by Roy (1958) and shown to have the composition quoted by Glasser and Roy (1959). Glasser *et al.* (1961) showed that a number of other synthetic calcium silicate hydrates were substantially the same as Roy's phase *Y*.

Here a single crystal, extracted from a thin section, gave an identical pattern on an oscillation photograph to a sample of phase *Y* synthesized by McConnell and on which the following cell constants had been determined: *a* 6·80 Å, *b* 6·91 Å, *c* 12·85 Å (all ±0·05 Å), α^* 88·42°.

Preliminary Ca and Si determinations with the electron probe give compositions differing somewhat from that suggested by Roy. The (OH) content, determined by difference, was significantly lower at 1–2 %. Possibly dellaite may contain some fluorine, or perhaps the (OH) content may vary with the temperature of formation in a manner similar to that suggested for Roy's phase *Z* by Taylor (1960). Certainly the refractive index data quoted by Glasser *et al.* (1961) which are quoted below do not rule out the possibility of a variable composition for this compound.

TABLE 1. Reactions and the mineral assemblages produced in the late stage replacement veins in metamorphosed limestones at Kilchoan. (The numbers refer to stability fields in fig. 1)

Vapour phase: H_2O and CO_2 both non-reactive
Kilchoanite → Wollastonite, (8).

Vapour phase: H_2O reactive, CO_2 non-reactive
Kilchoanite → Dellaite and Foshagite, (7).
Kilchoanite → Wollastonite and Foshagite, (9).
Kilchoanite → Foshagite, (9) or (10).
Merwinite → Foshagite, (9) or (10).
Larnite → Plombierite.
Ettringite (fissure veins only).

Vapour phase: H_2O and CO_2 both reactive
Spurrite → Dellaite and Calcite, (5).
Spurrite → Dellaite and Tilleyite and Calcite, between (5) and (6).
Kilchoanite → Foshagite and Spurrite (stable at lower total pressure).
Rustumite → Foshagite and Spurrite (stable at lower total pressure).
Spurrite → Scawtite and Calcite.

Vapour phase: CO_2 reactive, H_2O non-reactive
Wollastonite → Spurrite, (3).
Kilchoanite → Spurrite, (3).
Spurrite → Tilleyite and Calcite, (4).
Kilchoanite → Wollastonite and Spurrite, (3).
Kilchoanite → Tilleyite and Wollastonite, (6).

	Roy (1958)	Glasser *et al.* (1961)		McConnell	Dellaite, Kilchoan
α ...	1·650	1·640	1·642	1·652	1·650
β ...	1·661		n.m. 1·650	1·657	
γ ...	1·664	1·658	1·672	1·660	1·660
$2V$ ...	$< 30°$			$-60°$	$-65°$
	$\alpha' \wedge$ elong. 15°		$\alpha' \wedge$ elong. 10°		$\gamma' \wedge$ elong. 20°

At Kilchoan dellaite associated with calcite surrounds or veins resorbed spurrite and there has no well marked habit. In other cases it occurs as bladed crystals (with a different elongation to the synthetic mineral), with inclusions and matrix of calcite, as patchy veins in spurrite rich rocks. Dellaite, although fairly widely distributed, occurs only in very small amount. In any thin section in which it is present it usually occurs only in one small patch (1–2 mm) or vein.

Foshagite occurs as fibrous aggregates commonly perpendicular to the margin of the veins, with sharp contacts against merwinite, larnite, or kilchoanite. It is particularly common in veins traversing the latter mineral. The identity of the foshagite was confirmed by X-ray powder photographs, electron probe determination of Ca and Si, and from its optical properties: α 1·594, γ 1·598, $\gamma = c$, $+2V$ large, which are in agreement with Eakle's data (1952).

It is not impossible that other colourless fibrous calcium silicate hydrates are present, particularly mantling vein wollastonite. Hillebrandite and xonotlite were looked for but their presence could not be established.

Spurrite has normal properties. In monomineralic veins it may occur as crystals making the full width of a vein and elongated along the length of the vein. Where it is associated with other minerals it occurs in irregular intergrowths.

Tilleyite where it occurs as a vein mineral is distinguishable from spurrite by its optic sign and a marked development of lamellar twinning.

Wollastonite in monomineralic veins appears as a string of equant single crystals; in complex veins it is more commonly bladed and sheathed with a fibrous mineral. The latter is assumed to be foshagite as in some cases it is in optical continuity with established foshagite from the vein margin.

Scawtite occasionally occurs replacing spurrite as scaly aggregates, sometimes marginally to veins but more commonly to ettringite-filled or unfilled fractures traversing the rock.

Ettringite occurs in sharp fissure veins $< 0{\cdot}5$ mm. in width, which are the latest of all veins to develop. The fibrous crystals grow perpendicular to the vein wall and are locally altered to some mineral of very low birefringence.

Plombierite has occasionally been observed replacing larnite or merwinite in small patches not usually related to any vein.

General interpretation

In fig. 1 a qualitative attempt is made to plot the reactions inferred from a study of these metamorphosed limestones. The basis of the plot

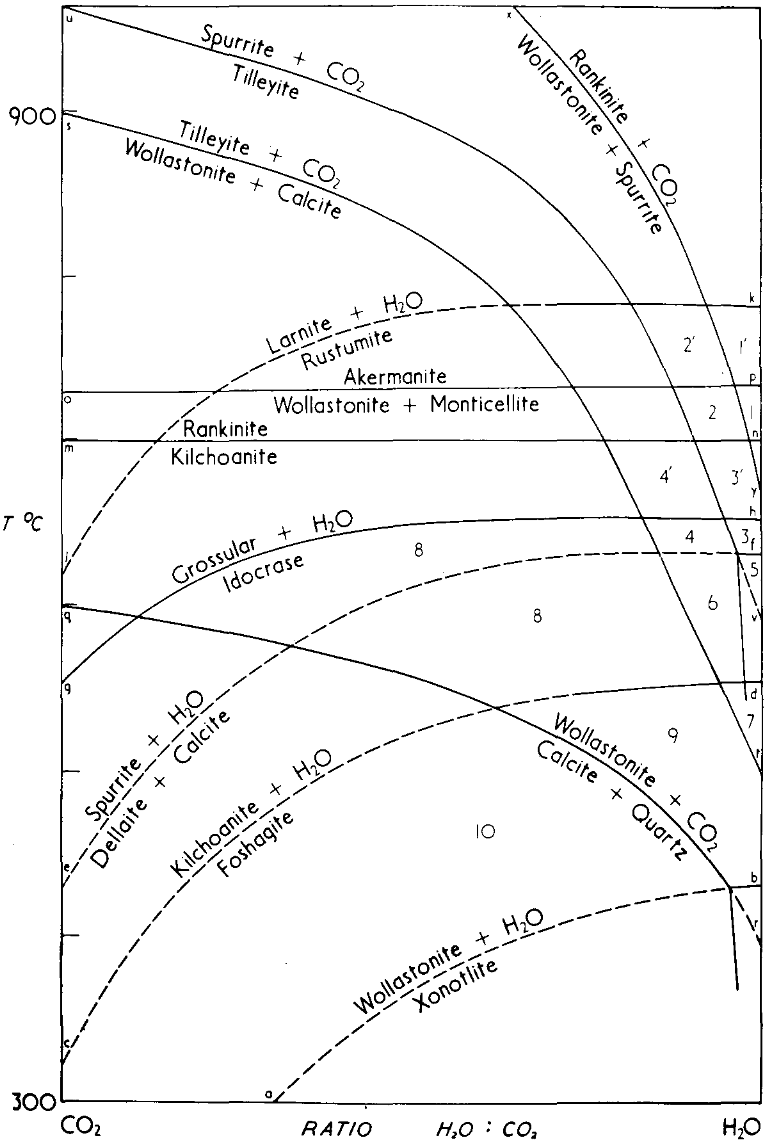

FIG. 1. An isobaric plot of temperature against the ratio of CO_2 : H_2O in the vapour phase, assuming P (H_2O+CO_2) = P (load). This illustrates schematically the stability fields of some of the minerals in the metamorphosed limestones at Kilchoan.

is an isobaric section of the petrogenetic model described by Wyllie (1962*a*, *b*) and illustrated by him with respect to the system $MgO–CO_2–H_2O$. In the present case most of the reactions fall in the system $CaO–SiO_2–H_2O–CO_2$.

The abscissa is the ratio of $CO_2:H_2O$, assuming $P\ (H_2O+CO_2) = P$ (load) here estimated at ±5000 lb/in^2. We have no experimental data for the composition of the mixed vapour phase for any of the illustrated reactions, so that the ratio of $CO_2:H_2O$ should only be considered in the most general sense of increasing or decreasing.

For the ordinate, temperature, experimental data at 5000 lb/in^2 are available for some of the reactions in limiting three-component systems, and for certain essentially solid-state transformations: e.g.

Xonotlite → Wollastonite + H_2O ± 400°C (Bruckner, Roy, Roy, 1960).
Kilchoanite → Rankinite ± 800° C (Roy, 1958), ± 700° C (McConnell, personal communication).
Calcite + Quartz → Wollastonite + CO_2 ± 600° C (Harker and Tuttle, 1956).
Calcite + Wollastonite → Tilleyite + CO_2 ± 920° C (Harker, 1959).
Tilleyite → Spurrite + CO_2 ± 970° C (Harker, 1959).
Wollastonite + Monticellite → Åkermanite ± 720° C (Harker and Tuttle, 1956).

For each reaction illustrated CO_2 or H_2O may only behave as a diluent up to a certain ratio in the vapour phase, so that every decarbonation curve should be cut off by an appropriate dehydration curve. Thus the reaction curve *rq* calcite + quartz → wollastonite + CO_2 is cut by the curve *ab* xonotlite → wollastonite + H_2O. In the present system where a reaction is considered metastable it is drawn as a dashed curve.

The fact that most calcium silicate hydrates are only stable with a vapour phase having a low $CO_2:H_2O$ ratio suggests that these intersections will be close to the H_2O side of the plot. A similar relationship has been observed by Wyllie (1962*a*, *b*) in the system $MgO–CO_2–H_2O$. Fluorine, as shown by small amounts of cuspidine and idocrase, is also present as a subsidiary component in the vapour phase. Its presence will not significantly alter the position of reaction curves to which it behaves as a diluent.

If one considers the progressive metamorphism of a calcite-quartz rock containing a small amount of water, wollastonite will first form at some point close to the low-temperature side of the curve *rq*. The CO_2 released will rapidly bring the vapour pressure up to the load pressure.

As CO_2 can now escape, further production of wollastonite will be tied to the reaction curve. As the CO_2 escapes it will continuously flush out the small amount of H_2O originally present in the rock, and as the temperature rises the vapour phase will rapidly approach pure CO_2 in composition. When all the quartz is used up the vapour phase remains approximately constant in composition with continued increase in temperature; though if the rock is permeable to any H_2O escaping from the igneous body the ratio of $CO_2:H_2O$ would decrease. When the temperature of the next decarbonation curve *st* is reached the reaction wollastonite + calcite → tilleyite + CO_2 will again build up the composition of the vapour phase to nearly pure CO_2. The final mineral assemblage that will be produced under a given pressure is dependent on the temperature and the initial composition of the rock. At Kilchoan these are the decarbonation assemblages listed.

With the fall in temperature following the initial phase of thermal metamorphism the pressure of the vapour phase will probably fall rapidly. This is because, unless there was free access of CO_2 or H_2O, the slightest retrograde reaction would utilize the vapour available in the body of the rock. If there was limited access of vapour derived from the adjacent intrusion at this stage of its cooling history, it would be dominantly H_2O, so that retrograde reactions would all be under conditions of a high ratio $H_2O:CO_2$ in the vapour phase. If $P\ (H_2O+CO_2) < P$ (load) such reactions as took place would have to be represented on another isobaric plane in the petrogenetic model.

At Kilchoan the reactions of a second phase of metamorphism fall into the following categories:

1. Production of (OH)-bearing calcium silicates, which was not possible in the initial metamorphism because of the high ratio of $CO_2:H_2O$ in the vapour phase:
   e.g. Dellaite, Rustumite
2. Inversion of minerals which were formed above a transition temperature in the initial metamorphism:
   e.g. Rankinite → Kilchoanite
3. Breakdown of minerals formed during the initial metamorphism:
   e.g. Åkermanite_{ss} → Wollastonite + Monticellite + Grossular.
4. Recrystallization of minerals produced in the initial metamorphism:
   e.g. 'Granular' Wollastonite → 'Porphyroblastic' Wollastonite
5. Production of small amounts of fluorine-bearing minerals:
   e.g. Cuspidine, Grossular → Idocrase.

Below are given the fields in fig. 1, in which some of these minerals are developed:

Rustumite—fields 1 and 1′

Paragenesis: stable-spurrite, rankinite;
unstable-larnite, merwinite;
sometimes stable sometimes unstable-åkermanite.

Rustumite may also be formed in fields 2 and 2′ but there is no evidence for the reaction rankinite + CO_2 → spurrite + wollastonite

Kilchoanite—fields 3 and 3′

Paragenesis: stable-spurrite, wollastonite;
unstable-åkermanite;
sometimes stable sometimes unstable grossular—idocrase.

The possibility of the instability of spurrite with a vapour phase containing some SiO_2 has been noted previously. At Camphouse, Ardnamurchan, the association of tilleyite with kilchoanite suggests that the ratio of $CO_2:H_2O$ was higher and characteristic of fields 4 and 4′.

Wollastonite—fields 1 to 4

Wollastonite, where associated with grossular and idocrase only, could recrystallize without the development of new minerals in these fields; grossular altering to idocrase on the low temperature side of *gh*.

The mineral assemblages in the late stage replacement veins may also be plotted on the same diagram if the pressure conditions have not changed unduly. The appropriate fields for their mineral assemblages are listed in table 1. For the veins a limiting feature is the general stability of idocrase as pseudomorphs after grossular, or recrystallized idocrase at the contacts of, or occasionally within the veins. It will be seen that in different veins H_2O or CO_2 separately or together may be reactive components and that some reactions also involve the accession or leaching of SiO_2 or CaO, e.g. kilchoanite → wollastonite ± foshagite, wollastonite → spurrite, kilchoanite → spurrite. The replacement of kilchoanite by spurrite falls in the same field as that in which, at an earlier stage in the metamorphic history, kilchoanite developed from rankinite ± spurrite. This is possible because the concentration of another component (CaO) in the vapour phase may alter the behaviour of CO_2 even though the ratio of $CO_2:H_2O$ remains unchanged.

The vein assemblages have been assumed to be in equilibrium but this may not be warranted. Metastable reactions may have taken place and the P, T, X conditions could have varied with time even in such a small scale feature. It is also possible that in a vein system initiated by fractures the total pressure might decrease very markedly; e.g. in fig. 1 as drawn, spurrite and foshagite have no common stability field. At lower ($H_2O + CO_2$) the curve *uv* might be sufficiently displaced to cut the curve *cd* and a field for a stable association be developed.

Conclusions

It has been shown that the metamorphosed limestones at Kilchoan show a succession of mineral assemblages: first a decarbonation series and second a superimposed hydration series terminated by a system of minor replacement veins.

The initial decarbonation assemblages are comparable to those produced at several other Tertiary dolerite or gabbro-limestone contacts, e.g. Scawt Hill, Ballycraigy, Camasunary, Blaven, Camphouse, Camas Mor, and Barnavave.

At these contacts retrograde changes are restricted because of lack of access of H_2O and CO_2 in the cooling stage of their thermal history. However, associated with the larger and more deep-seated intrusions, limited retrograde reactions occur. In these some of the minerals developed are identical with those at Kilchoan even to the extent of rankinite being partially replaced by kilchoanite.

At Kilchoan the later mineral assemblages of the hydration series and the associated veins could be considered as retrograde assemblages, end products of a single thermal cycle, initiated by either the porphyritic dolerite of Glas Bheinn or the quartz gabbro of Centre 3. However, it would be remarkable if this narrow (±200 ft) screen had escaped initial metamorphism by the Glas Bheinn intrusion or showed no superimposed effects due to the later quartz gabbro. The unique mineralogy also suggests that the history here has been significantly different from the contacts noted above, where the aureoles were developed during a single thermal cycle.

The preferred interpretation is that the initial decarbonation assemblages at Kilchoan, developed under conditions maintaining a high $CO_2:H_2O$ ratio in the vapour phase, were due to the thermal effect of the porphyritic dolerite intrusion. Subsequently these rocks were re-metamorphosed by the quartz gabbro.[1]

[1] It should be noted that at the Blaven contacts retrograde assemblages are

This second phase of metamorphism operated on material which had been fully decarbonated, so that no reactions were possible which would liberate CO_2. Because of this the limited amount of water released from the crystallizing quartz gabbro magma was able, in those portions of the aureole that were permeable, to build up a very high ratio of $H_2O:CO_2$ in the vapour phase. At temperatures of about 600–750° C some of the original minerals became unstable or recrystallized, producing the rustumite, kilchoanite, idocrase, breakdown products of melilite, or the porphyroblastic wollastonite which have been described.

It should be noted that Roy (1958) ascribed the absence of phases X (Calciochondrodite), Y (Dellaite), and Z (Kilchoanite) to the high ratio of $CO_2:H_2O$ normally present in the vapour phase of thermally metamorphosed limestones. Of these compounds only calciochondrodite has not been observed at Kilchoan; it is not unlikely that continued search will reveal its presence.

The latest events associated with the metamorphism by the quartz gabbro are represented by intermittent fracturing of the rocks and the associated development of replacement or fissure veins. These replacements are retrograde in that the mineralogy indicates a general falling temperature sequence in which the $H_2O:CO_2$ ratio varied in the vapour phase. It is at this stage that dellaite develops at the expense of spurrite. It is evident in certain cases that CaO and SiO_2 were introduced. It is probable that the SiO_2 and H_2O were derived from the crystallizing magma, whereas CaO and CO_2 were picked up by the vapour as it traversed the calcitic portion of the limestone sequence. The range of temperatures covered by the veins was from ±600° C, through ±300° C (a possible lower limit for the formation of foshagite) to ±100° C or whatever temperatures may have been maintained in the slowly cooling volcanic pile.

There is very little evidence for the actual ratio of $H_2O:CO_2$ in the vapour phase associated with the second phase of metamorphism. The impression is that it was normally very high, but this can only be confirmed by experimental studies on the stability of the observed minerals in the presence of CO_2 and H_2O.

The possibility of the production of calcium silicate hydrates in the earliest stages of metamorphism of siliceous limestones is not impossible and should be looked for in rocks associated with those in which wollastonite is just being developed. They will however be difficult to

more extensive than at the other examples cited, and this may be correlated with the presence of granophyre intrusions nearby (Wyatt, 1952).

distinguish from retrograde products formed at the expense of wollastonite.

Finally, it should be emphasized that many of the observations used in constructing such a phase diagram as fig. 1 are subjective and that petrographic inspection can at the best only be given a qualitatively correct representation. Though the rocks themselves may yield modifying data, it is only by experimental studies that a quantitative diagram can be drawn.

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