# PHYSICO-CHEMICAL ANALYSIS OF MINERAL PARAGENESIS IN ZONED SKARNS.

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Looking up into the sky one sees the celestial bodies moving along defined orbit. And down in the realm of rocks and minerals a certain pattern prevails, No matter what is the cause or wetner it has any, the order is significant.

## *ICHTISAR*

1) *Proses metasomatis jang merupakan proses dimana terlibat perubahan komposisi kimia setjara keseluruhan (bulk composition) dari kelompok² mineral teertentu (mineral assemblage) ternjata dapat diterangkan dengan prinsip² "phaserule" dari Gibs adn ada hubungannja dengan thermodynamica.*

2) *Proses metasomatis mengeluarkan mineral jang karakteristik dan stabil dimana konsep dari "mineral facies" dapat dipakai.*

## I. INTRODUCTION

1. Since Goldschmidt published his „*Kontactmetamorphose des Kristiana-Gebietes,*" much attention has been given to the formation of zoned skarns in contact aureoles of granitic and granodioritic rocks and limestones, and this paper will partly give an illustration of several zonal arrangement of skarn rocks, and partly about the facies classification and the physico-chemical analysis of the mineral paragenesis.

2. Progressive replacement of limestone inclusions in granite at Ballynacarrick Co., Donegal, is reported by Gindy (1950). He mentioned the occurrence of a skarn armour made up of definite mineral zones in limestone inclusions in granite. From the granite intrusive outward, zones of hornblende or diorite, plagioclase, pyroxenes, clinozosite and grossularite (with or without idocrase) have been observed in successive order. The replacing nature of the grossular and idocrase of the marble is microscopically to be seen. Idocrase replaces the diopside calcite mosaic as well as any grossular that may have formed in it. According to Gindy, it is impossible to solve the time-relationship between grossular, idocrase and wollastonite. His opinion is namely that these minerals were formed roughly at the same time, their order of production being

dependent both on the composition of the diffusing material (and this is neither constant in time nor in different parts of the limestones) as well as upon the different rates of diffusion of the various ions.
These different zones are not "static", but move into the limestone, each replacing the one preceding it and being replaced by the zone following it. See Fig. 1.

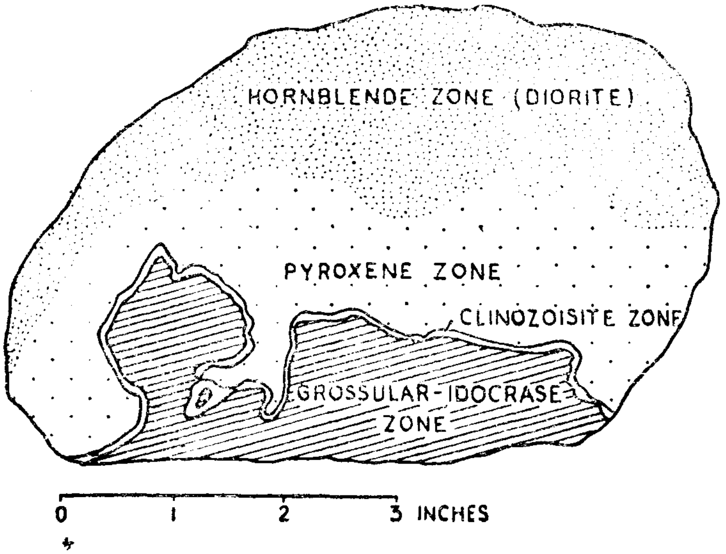


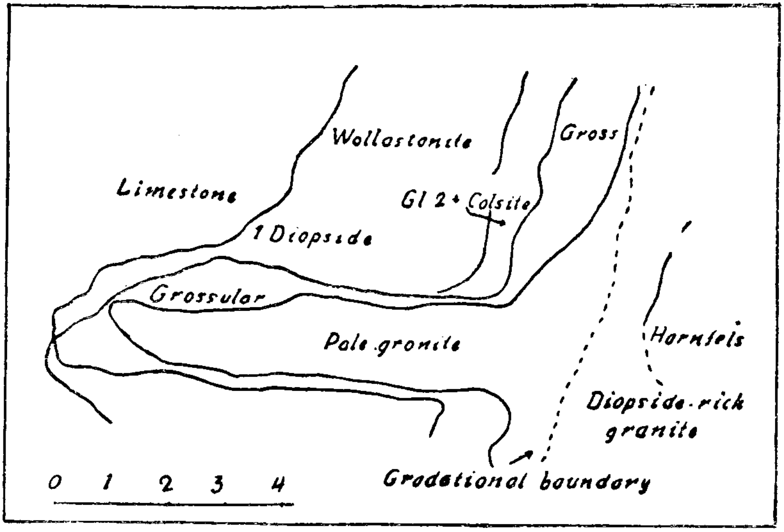
*Fig. 1 Different mineral zones in the skarn of Ballynacorrick.*

Gindy concluded that it is due to the physico-chemical conditions that the difference in mineralogical constitution and order of the different zones of the skarn armour are formed.

3. Zoned skarns are also reported from granite-marble contacts near Puyvalador by Waters, (1957), in the Quericut area, eastern Pyrenees. Waters came to the conclusion that contact metamorphism of the limestones and calcarecus siliceous rocks during granitic intrusion was followed by metasomatic replacement of the marble, which produced the up to 10 cm zoned skarns. Under pneumatolitic conditions interchange of silica, alumina and lime should have taken place between granite and marble. He also described the occurrence of zoned wollastonite-grossular-clinozoisite skarns at the contact. Beside these 3 main characteristic minerals he noticed the presence of diopsides (constantly present though in small amount), phrenite (very uncommon),

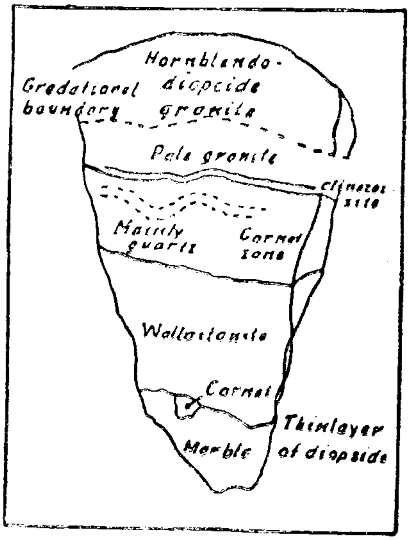
idocrase (widely distributed, though in small amount), hornblende (associated by epidote, calcite, pyrrhotine and minor plagioclase and microcline). See Fig. 2 and Fig. 3.

Fig. 2



Sketsch of zoned skarn contact in Quericut area

Fig 3



Sketch of zoned Contact
(Puyvalador)

The formation of clinozoisite was described to the accumulation of volatiles in the crystalizing modified granite. The presence of this mineral indicates to the author of relatively high pressure.

4. Another example of a zoned skarn is the one described by Burnham (1959) from Crestmore, in California. Here, a plutonic mass of quartz diorite, and a relatively small pipe like hypabyssal mass of quartz diorite, and a relatively small pipe like hypabyssal mass of quartz monzonite porphyry intruded into the magnesian marbles and caused the formation of several zoned skarns.

   The exomorphic effects of the carbonate rocks, which has been engulfed partly by quartz diorite can be seen as :

   a. formation of 30 cm thick metasomatic silicate contact rocks composed of diopside, wollastonite and grossularite.

   b. a conversion of nearly all the magnesian-bearing carbonate beds to periclase marbles.

      The younger quartz monzonite porphyry injected into the marble is nearly all contaminated on account of reactive assimilation, giving rise to a 15 meter thick aureole with the following mineral zones :

   c. garnet zone (grossularite, wollastonite, diopside — in decreasing amount.

   d. idocrase zone (idocrase only).

   e. monticellite zone (mainly monticellite in association of clinohumite, cuspidine, ellestadite, forsterite, melilite, merwinite, peruvskite, spurrite, tilleyite, xantophyllite). See Fig. 4.

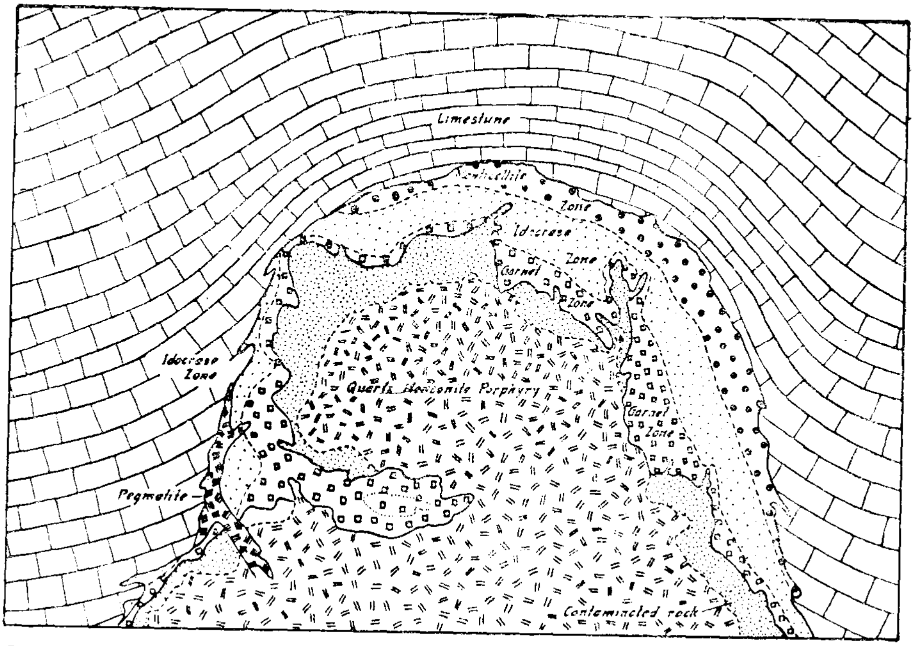


Fig 4 Idealized North-South cross section (Not to scale) through Quartz Monzonite Porphyry intrusion (Crestmore).

The chemical composition of three zones is given in Table I, Table II, and Table III. From the difference in chemical composition in the three zones, the accompanying mineralogic differences can be seen.

The atomic ratio $\frac{Si}{Ca + Mg}$ in the monticellite zone is 1 : 2
in the idocrase zone 1 : 1.5
in the garnet zone 1 : 1

Zonation of mineral assemblages reflects a corresponding zonation in the bulk chemical composition in the rocks, as shown by the changes in the ratio of metasomatic to indigeneous constituents (Si + Al + Fe) (Ca + Mg) from 0.66 in monticellite zone, 1.15 in idocrase zone and 1.62 in garnet zone.

Also in the monticellite zone itself a tendency of zonation can be seen. In the silica poor and calcite rich part: clinohumite, forsterite, spurrite, and spinel are concentrated; and in the silica rich innerpart, merwinite, cuspidine, mililite are concentrated.

## II. PHYSICO-CHEMICAL ANALYSIS OF THE MINERAL PARAGENESIS AND METAMORPHIC FACIES OF THE SKARN ROCKS.

5. From the above description it is clear that the number of minerals in zoned skarns in contact aureoles of granitic/granodioritic rocks and limestones/marbles are limited. Besides, there are typical minerals which are constantly found such as wollastonite, diopside, grossularite, etc. The question is now, what are the factors which control this mineral assemblage ?

6. Already in 1912 Goldschmidt using Gibb's phase rule, $F = c + 2 - p$ (announcing that the number of stable minerals in a rock shall not be larger than the number of components) succeeded in showing that from alumina, lime, ferromagnesia, seven minerals will form that are stable under the conditions of contact metamorphism. The minerals are andalusite ($Al_2SiO_5$), cordierite ($Mg_2Al_4Si_5O_{18}$), anorthite ($CaAl_2Si_2O_8$), hypersthene ($(Mg,Fe)\ SiO_3$), diopside ($Ca\ (Mg,Fe)\ Si_2O_6$), grossularite ($Ca_3Al_2Si_2O_8$), hypersthene ($(Mg_1Fe)\ SiO_3$), diopside ($Ca\ (Mg,Fe)\ Si_2O_6$), grossularite ($Ca_3Al_2Si_2O_8$), wollastonite ($CaSiO_3$) See Fig. 5.

7. Natural hornfelses very closely follow this theoretical mineral association, which shows that a state of chemical equilibrium is approached. However, nonadjustment of equilibrium does occur in connection with special geological conditions. When pure calcareous sediments come in contact with effusive rocks where high temperature prevails for a short time only and cooling is rapid, anomalous mineral assemblages can be formed with rare mineral species, some of which have to be regarded as metastable forms and some as high temparature forms such as melilite, fossaite, merwinite, larnite, scawtite, spurrite, rankinite, monticellite and perovskite.

8. Igneous intrusion does not provide high temperature and pressure only but the accompanying magmatic gas phase will provide water and other

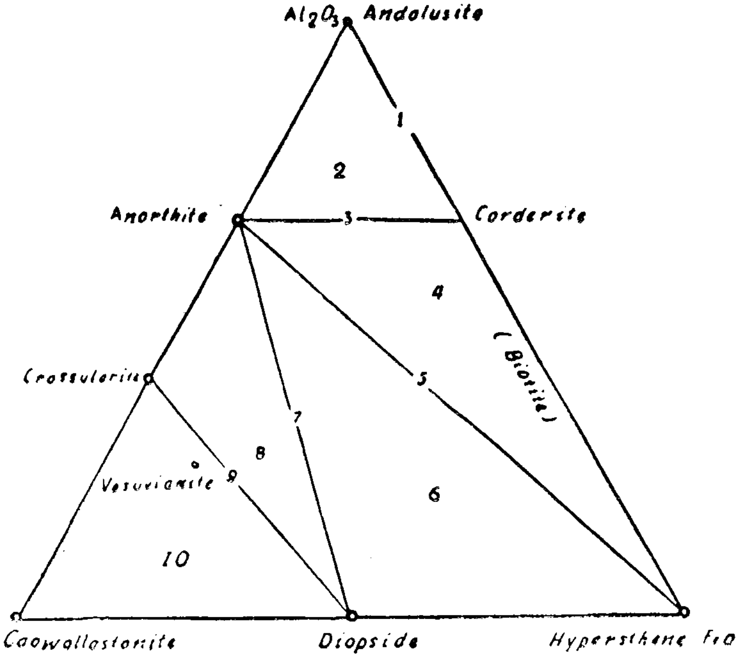


Fig. 5

volatile compounds resulting in pneumatolysis and metasomatism. The primary magmatic gases are acid and show in consequence high reactivity. If the contact rock is basic (limestone/marble) the acid gases will react effectively with it. Limestone therefore reacts as a filler, capturing the escaping gases with the formation of a great variety of reaction minerals; the corresponding rocks are known as skarns.

9. Thompson (1955) made a remark that in a metasomatic assemblage the content with respect to certain components is related to enviromental conditions rather than to an initial bulk condition. The chemical potential of these components will be fixed by environtal conditions. In an assemblage occupying a finite volume we should expect that these chemical potentials would in general vary from point to point, independently of pressure and temperature.

10. In a metasomatic process, with the equilibrium factors T, V, a, Uf Uk and under constant external condition, T, Uf, ... Uk, with Jin =Cm + 1. The state of the system is completely defined by the values V, a, b, ... c. And we have:
$f_{\text{inter}} = f_{T,\ \mu_m} = C_1 + C_m + 2 - p - J_{in} = C_1 + 1 - p.$
So the maximum number of coexisting minerals here (with arbitrary conditions) is $C_1 + 1$ since with this number the system becomes invariant ($f_{\text{inter}} = 0$) Korzhinsky, (1957). Usually one of a perfectly minerals in the system is composed only of the perfectly mobile component (It is deposited from pure solutions and occupies vacant spaces in rocks). The change of the total volume in the presence of a perfectly mobile mineral changes the content of the latter only and does not affect

other parameters of the system and in particular, the composition of the minerals. The inert components control the system, except for the perfectly mobile mineral. So, each paragenesis in the system with three inert components, may contain also a mobile mineral. And in the metasomatic process it is quartz or calcite.

Korzhinsky, (1957) stated that at each front of replacement there should occur a complete replacement of one of the minerals, independently of the volume relations. Further he stated that coexistence of two polymorphic forms is not caused by the restriction of volume. The possibility for the coexistence of two such forms is only under definite pressure for a given temperature, while in metasomatism the pressure on minerals is controlled by the concentration of solution.

11. Metasomatic rocks have very characteristic and stable mineral association. So, the author of this paper is fully convinced that the facies principle can be applied notwithstanding the fact that it is impossible to classify all the mineral assemblages of the skarn rocks into one metamorphic facies, which is according to the author a proof that the mineral assemblages of all zoned skarns are not originated under the same condition, and he suspects that any zoned skarn represents a rather narrow pressure-temperature range.

12. The skarn rocks with the mineral assemblage : grossularite-wollastonite-diopside in Crestmore and Puyvalador should be grouped into the pyroxenehornfels facies defined by Fyee-Turner-and Verhoogen (1958) See Fig. 6. The exomorphic effect of the quartz diorite on the carbonate rocks chracterises high $P_{co_2}$. Also highly temperature prevails. This mineral assemblage also belongs to the hornbende hornfels facies, but the absence of micas and amphiboles exclude it from this facies. The garnet zone with wollastonite, diopside, grossularite is clearly formed at the expense of the rocks of the idocrase and monticellite zone. Table II shows that (Si + Al + Fe)/(Ca + Mg) =1.4 X as large in the idocrase zone,

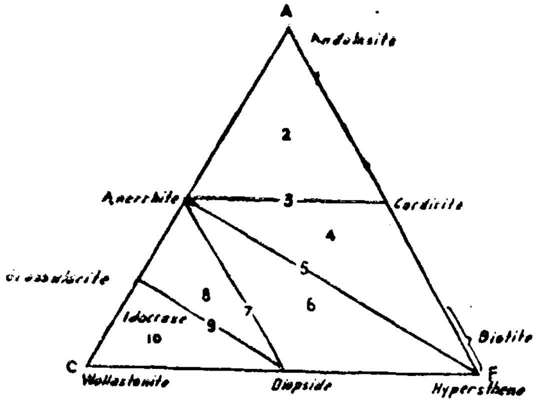


*Fig. 6 Pyroxene hornfels facies. ACF-diagram for rocks excess in silica.*

and 2.5 X as large as the monticellite zone. $Ca_{10}Mg_2Al_4Si_9O_{34}(OH)_4 + 3\ SiO_2 \longrightarrow 3\ Ca_3Al_2SiO_3O_{12} + 2\ CaMgSi_2O_6 + 3\ CaSiO_3 + H_2O$
(1 idocrase + 3 silica ⟶ 2 grossularite + 2 wollastonite + 2 diopside + 2 water) ;
Addition of silica to monticellite only produces the 3 minerals of the garnet zone.

13. On the other hand the mineral assemblage described by Gindy from Ballynaccarick has to be classified into hornblende-hornfels subfacies of the almandine amphioblite facies (see Fig. 7). This facies is typical for high grade zones of progressive metamorphism. In this contact rocks as well as in those of Puyvalador the presence of clinozoisite is very common, and according to the author of this paper, this is an indication of relatively low temperature and high $P_{H_2O}$ at the contact.

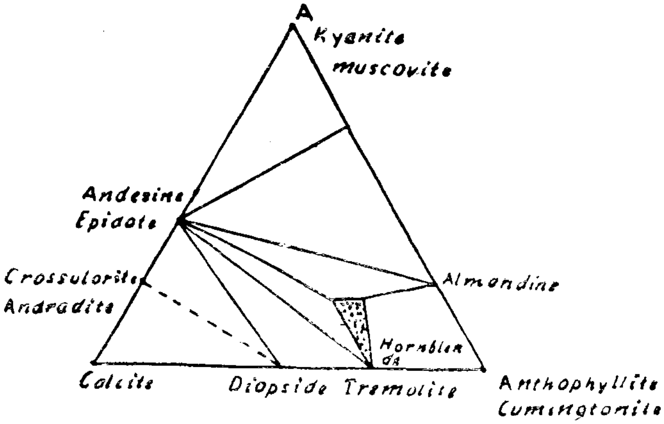


Fig 7 Almandine amphibolite facies, Staurolite Quartz Subfacies ( Excess $SiO_2$ )

14. The mineral assemblages in the monticellite zone at Crestmore are rather complicated. They should be grouped into the Sadinite-facies. The combinations : monticellite-forsterite-calcite and monticellite-merwinite-melilite indicate *rather high temperatures,* while monticellite-merwinite-melilite ; merwinite-spurrite-calcite and merwinite-monticellite-calcite indicate *very high temperatures.* For the formation of these minerals these following reactions are suggested :

1) 9 bruccite + 4 silica ⟶ 1 clinohumite + 8 water,
2) 2 clinohumite + 1 silica ⟶ 9 forsterite + 2 water,
3) 1 forsterite + 2 calcite + 1 silica ⟶ 2 monticellite + 2 carbondioxide.
4) 5 calcite + 2 silica ⟶ 1 suprrite + 4 carbondioxide.
5) 1 spurrite + 1 carbondioxide ⟶ 1 tilleyite
6) 4 spurrite + 2 silica + 5 water ⟵ 5 cuspidines + 4 carbondioxide
7) 5 monticellite + 2 spurrite + 1 silica ⟶ 5 merwinite + 2 carbondioxide.

8) 1 brucite + 1 allumina $\rightleftarrows$ 1 spinel + water.

9) 2 spinel + 1 calcite + 1 silica + water ⟶ 1 xanthophillite + 1 carbondioxide.

10) 10 calcite + 2 magnesia + 3 alumina + 7 silica ⟶ 3 melilite + carbondioxide.

Fig. 8 gives the petrological relation between and within the zones. Introduction of silica and alumina and removal of magnesia is represented by the passage from M→I (Fig. 8). Here is a clear picture of the "flood" of silica and alumina outward the intrusive mass.

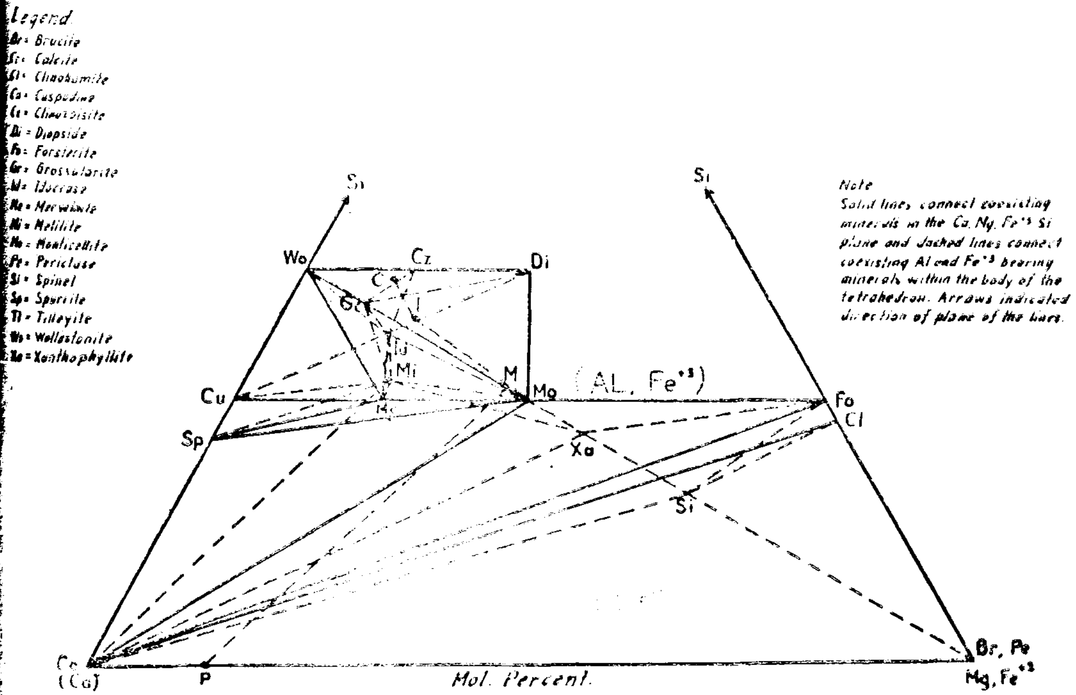


Fig. 8 Tetrahedral composition diagram for part of the system Ca-Mg, $Fe^{+2}$ - Si - Al, $Fe^{+3}$ The Al, $Fe^{+3}$ apex is at the eye of the observer. Only those minerals that occur in the contact aureole of crestmore are represented (Burnham).

15. *P — T problem in the formation of wollastonite.* During the high temperature metaporphism, calcite and quartz become unstable and react to produce wallastonite and $CO_2$. The P—T curve of Goldschmidt (Fig.9) shows that at 5000 atm. which corresponds to a pressure at a depth of 20 km, the temperature of reaction is almost 9.000° C ($P_{CO_2}$ = pressure on rock). But in most cases rocks are permeable to $CO_2$, which therefore escapes from the locale of reaction.

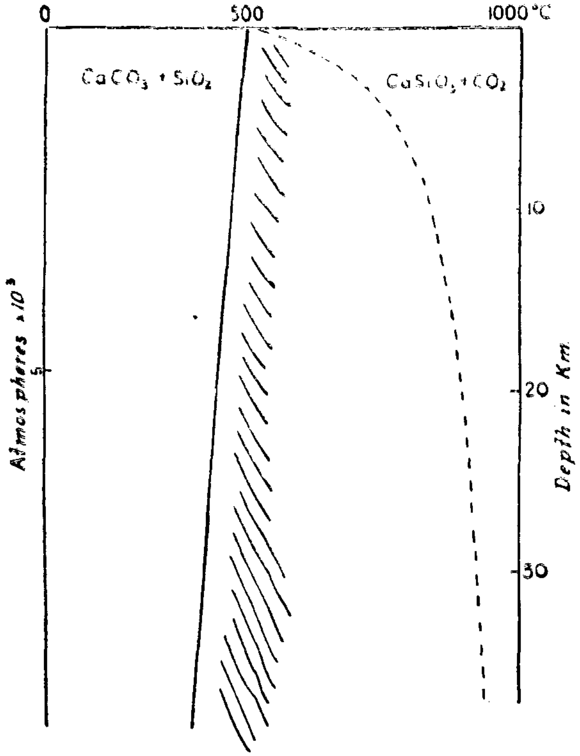


*Fig. 9 The change of the temperature of the reaction $CaCO_3 + SiO_2 = CaSiO_3 + CO_2$ with pressure. Stippled line: Curve after V. M. Goldschmidt (Vid. Selsk. Str. I. Kristiania, 1912) valid only in a closed system of constant pressure. Full line: Curve for an open system in which carbon dioxide is removed. In most rocks the conditions will lie close to the full line, prubably in the hatched area.*

If gas is enabled to escape, the molecular volume of the gas can be neglected. By means of the equation of Clapeyron :

$$\left.\begin{array}{l} \left[\dfrac{\partial \ln k}{\partial p}\right]_T = \dfrac{\wedge V}{RT} \\[2ex] \left[\dfrac{\partial \ln k}{\partial T}\right]_P = \dfrac{\wedge H_2}{RT} \end{array}\right\} \quad \frac{dT}{dP} = \frac{T}{\wedge H}\left((V - V').\right)$$

The change in the temperature of reaction and pressure can be computed. If only the volumes of the solid phase is considered and if the molecular volume is expressed in cm$^3$ :

$$CaCo_3 + SiO_2 \rightarrow CaCo_3 + Co_2,$$
$$22 \qquad 37 \qquad\qquad 41$$

$$\text{and} \quad \frac{dT}{dP} = \frac{VT}{Q} = \frac{18 \times 720}{10^6} = 0.0013 \text{ degree/atm.}$$

If $CO_2$ is effectively removed as soon as it forms, the differential pressure will squeeze $CO_2$ out of calcite at lower temperature than is otherwise possible.

So, instead of being impeded, the formation of wollastonite will be facilitated by the increase of temperature.

Fig. 10 shows that calcite and quartz are stable together up to 600° C at 300 pounds/inch$^2$. $CO_2$-pressure, Harker and Tutle, (1956), while wollastonite and calcite remain stable together up to 1000° C at the same pressure ; the 400° C difference in T between the appearance of wollastonite and that of spurrite is reflected in the common occurrence of the former at granite-limestone contacts and of the latter — at diabase — limestone contacts. The rare occurrence of spurrite in granite/limestone contacts indicates that $P_{CO_2}$ is relatively high and may well be commensurate with rock load.

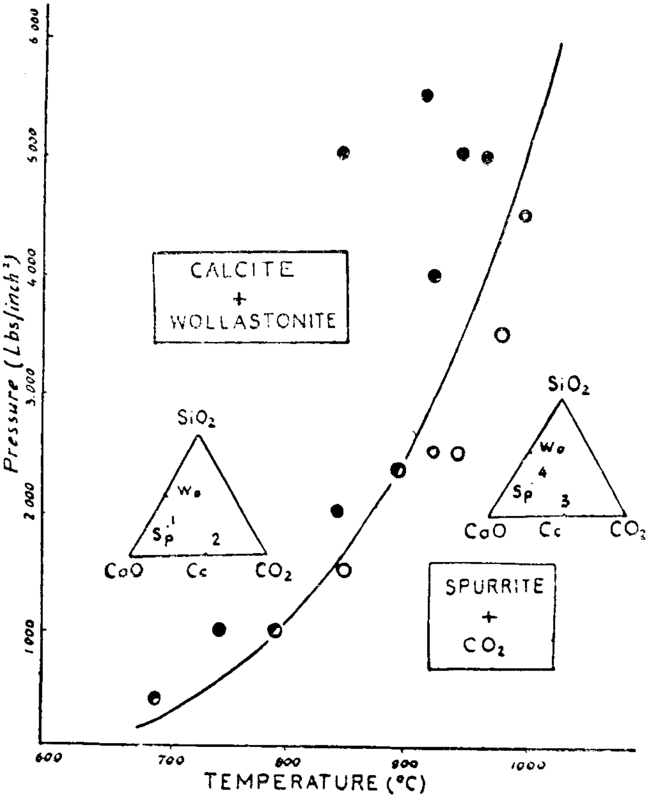


*Fig. 10 Pressure ($CO_2$) temperature curve for univariant reaction $3CaCO_3 + 2CaSiO_3 \rightleftharpoons 2Ca_2SiO_4 . CaCO_3 + CO_2$ Wo = Calcite, Sp = Spurrite.*

The vapour phase should be rich in $CO_2$, as presence of $H_2O$ would lower partial pressure of $CO_2$ permitting calcite and wollastonite to react to give spurrite.

## III. CONCLUSION

(1). Metasomatism which the author defines as any process involving a change in the bulk composition of the mineral assemblage, still can be approached by means of the phase rule of Gibs and other thermodynamic relationship.

(2) Metasomatism also yields very characteristic and stable type of mineral associations to which the concept of mineral facies can be extended.

(3) Limestone metasomatism described in I, proves that in the formation of the skarn, silica and alumina have been added to the marble from the granite and that lime has been moved out of the marble from the granite.

(4) Apparently, the mineral assemblage in Crestmore does not correspond with Bowen's (1940) 13-steps in contact metamorphism (sequence and mode of origin).

An explanation can be looked for in two possibilities:

1) either that this assemblage is a nonequilibrium one or

2) that Bowen's sequence is wrong.

The author of this paper is more inclined to the opinion that Bowen's sequence is wrong.

What happens in small experimenting crucibles in the lab. does not necessary represent the real process in nature at large. There is one factor which experimental petrologists can never immitate, that is the factor "space and time".

(5) The two differences in mineral composition in Crestmore can be attributed to differences in pressure-temperature during intrusion.

(6) Description in I, and further physico-chemical consideration leads to the conclusion that one has to deal with a progressive metasomatism with consequent decarbonation at elevated temperatures rather than progressive decarbonation attendant simply upon rising temperature.

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TABLE I. Chemical Composition of Garnet-Zone Rocks
(Weight per cent)

| Constituent. | 1 | 2 |
|---|---|---|
| $Si0_2$ | 42.89 | 41.91 |
| $Ti0_2$ | 0.52 | 0.50 |
| $Al_20_3$ | 10.07 | 10.02 |
| $Fe_20_3$ | 8.14 | 5.28 |
| $Fe0$ | 1.82 | 0.75 |
| $Mn0$ | 0.22 | 0.11 |
| $Mg0$ | 2.43 | 3.67 |
| $Ca0$ | 32.39 | 36.28 |
| $Na_20$ | 0.24 | 0.00 |
| $K_20$ | 0.13 | 0.00 |
| $P_20_5$ | 0.11 | 0.13 |
| $H_20+$ | 0.75 | 0.80 |
| $H_20-$ | 0.04 | 0.00 |
| $C0_2$ | 0.80 | 0.36 |
| S | 0.04 | 0.04 |
| $S0_3$ | 0.00 | 0.00 |
| F | 0.02 | 0.02 |
| Cl | 0.00 | 0.00 |
| $Ba0$ | 0.00 | 0.00 |
|  | 100.43 | 99.87 |
|  | 0.02 | 0.02 |
|  | 100.41 | 99.85 |

TABLE 2. Chemical Composition of Montizellite Zone Rocks.
(Weight per cent)

| Constituent. | 1 | 2 | 3 |
|---|---|---|---|
| $Si0_2$ | 36.92 | 33.59 | 37.69 |
| $Ti0_2$ | 0.19 | 0.13 | 0.20 |
| $Al_20_3$ | 2.01 | 7.40 | 2.57 |
| $Fe_20_3$ | 1.59 | 0.80 | 2.75 |
| Fe0 | 2.57 | 2.28 | 1.14 |
| Mn0 | 0.19 | 0.11 | 0.07 |
| Mg0 | 20.24 | 20.37 | 10.54 |
| Ca0 | 32.70 | 32.66 | 37.73 |
| $Na_20$ | 0.04 | 0.06 | 0.07 |
| $K_20$ | 0.00 | 0.00 | 0.02 |
| $P_20_5$ | 0.03 | 0.02 | 0.15 |
| $H_20$ + | 1.05 | 0.62 | 1.00 |
| $H_20$ — | 0.15 | 0.27 | 0.42 |
| $C0_2$ | 1.75 | 2.00 | 6.10 |
| S | 0.00 | 0.00 | 0.00 |
| $S0_3$ | 0.13 | 0.13 | 0.15 |
| F | 0.00 | 0.00 | 0.02 |
| Cl | 0.00 | 0.00 | 0.01 |
| Ba0 | 0.04 | 0.00 | 0.00 |
| Total ...................... | 99.60 | 100.44 | 99.63 |
| Less 0 for F and Cl ...... | | | |

TABLE 3. Chemical Composition of Idocrase-Zone Rocks and Minerals.

(Weight per cent).

| Constituent. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $Si0_2$ | 39.68 | 41.70 | 37.41 | 9.62 |
| $Ti0_2$ | 0.48 | 0.54 | — | — |
| $Al_20_3$ | 9.49 | 9.67 | 17.89 | — |
| $Fe_20_3$ | 3.19 | 4.14 | 3.16 | — |
| Fe0 | 1.14 | 0.78 | 0.47 | — |
| Mn0 | 0.07 | 0.10 | 1.52 | 0.77 |
| Mg0 | 6.77 | 3.01 | 4.80 | — |
| Ca0 | 34.49 | 38.00 | 33.78 | 54.44 |
| $Na_20$ | 0.09 | 0.00 | 0.35 | — |
| $K_20$ | 0.00 | 0.00 | — | — |
| $P_20_5$ | 0.15 | 0.17 | — | 20.85 |
| $H_20$ + | 1.05 | 0.90 | 0.62 | tr |
| $H_20$ — | 0.01 | 0.03 | — | tr |
| $C0_2$ | 2.85 | 0.84 | — | 2.10 |
| S | 0.05 | 0.03 | — | — |
| $S0_3$ | 0.00 | 0.00 | — | 12.28 |
| F | 0.02 | 0.03 | — | — |
| Cl | 0.00 | 0.00 | — | — |
| Ba0 | 0.00 | 0.00 | — | — |
| Total ............. | 99.53 | 99.94 | 100.00 | 100.06 |
| Less 0 for S and F | 0.02 | 0.02 | | |
| | 99.51 | 99.92 | | |