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# PHASE EQUILIBRIA IN CALC-SILICATE HORNIII LEWIS AND CLARK COUNTY, MONTANA

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#### Abstract

Siliceons dolomites are progressively metamorphosed through the "all-degrees" "hornblende" and "pyroxene granulite" facies around a granitic stock 12 metabolic Lincoln, Lewis and Clark County, Montana. Contrasting initial composition and adjacent carbonate-rich beds gave rise to many irregularities in this progresses a informative reaction relationships at bed interfaces.

These relationships and application of the phase rule, which is faciliatated for the **\*** approximation of many of the beds to the CaO-MgO-SiO<sub>2</sub> system, indicate (1) that we equilibrium was attained within beds but that chemical potential gradients of **\*** and **\*** inert" components existed across bed interfaces, (2) that low-variant as a second common, but that assemblages with large variance predominate, and (3) that the volatile content determined in part the derived metamorphic assemblages.

Data on the composition and mineralogy of the Helena dolomite outside the research allow inferences concerning the specific reactions by which the metamorphic access the evolved. In addition, rough limits on the temperatures and total volatile president of these reactions occurred can be estimated by a combination of field, petrophysical experimental data.

## INTRODUCTION

Application of the Gibbs phase rule to problems in metabolic petrology has furnished much information concerning condition metamorphism, particularly with regard to the behavior of volume Such application, as recently reviewed by Zen (1963), is dependent proper identification of all minerals in a given assemblage, on the terms relations between the minerals, and on the compositions of the topoloand whole rock. Such data were obtained through petrographic and diffraction and partial chemical analytical studies of a systemetic collected suite of hornfels around an epizonal granitic stock in the two Mountains of west-central Montana.

Because of the small grain size of these hornfels and the sieve test of many of the minerals, particularly of the diopside and the simineral separations are practically impossible. Thus, the study as mainly on the absence or presence of minerals and on texture its rather than on the composition of co-existing minerals. However, compositional simplicity of many of the beds allows relatively inferences concerning the attainment and conditions of equilabparticular, the carbonate beds closely approximate the Catter system and the argillaccous beds may be interpreted in the CaO-MgO-SiO<sub>2</sub>-KAIO<sub>2</sub> system.

The data bears particularly on the interpretation of COLLERENT

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## EQUILIBRIA IN CALC HORNFELS

 $x_{2} = \pm x_{2}$  value" or "initial value" components (Zen, 1963) in an epiterm sometant metamorphic environment. The limitations of the phase  $x_{2} = x_{2}$  detaining such information have been reviewed most recently by  $y_{2} = x_{2}$  and Fyfe (1964).

We Helena dolomite (Knopf, 1950), from which the hornfels were nerected consists largely of rhythmically interlayered argillaceous and accounter quartz beds on a hand specimen level. At some places these states have be traced directly into the aureole. Such localities allow direct out stream of metamorphic assemblages in beds of contrasting composition shach were subjected to the same temperatures and total volatile gate test. Particularly interesting and informative in this regard are be a constructed at the boundaries of such beds and their indications of the set of effects at the boundaries of such beds and their indications of the set of effects at the boundaries under the influence of compositional gate ats

For study of the hornfels from western Montana was suggested by 456 - 15 (1907) detailed study of contact metamorphism around the 566 - value stock, located a few miles southeast of the area described here.

### GEOLOGIC SETTING

Granite Peak stock is about 12 miles east of Lincoln, Lewis and exclounty, Montana, and is but one of many late Cretaceous or early 7 may epizonal intrusions on the north side of the Boulder batholith excell, 1907; Pardee and Schrader, 1933; Knopf, 1913, 1950, 1957, peak

The stock, which was emplaced by magmatic stopping, is about  $1\frac{1}{2}$ in each diameter and occurs in one limb of a broad fold involving the broad matrix. The structure around the stock is thus relations simple as shown schematically by Fig. 1. Little or no doming the panied intrusion of the stock. Only the area from which most of the tracked samples were collected is shown in Fig. 1. The details concerning the statute of the area, and petrography and mode of emplacement of the tracked and nearby stocks are discussed as part of the general tables of the Lincoln area (Melson, 1966).

opt where adjacent to the stocks, the Helena dolomite is essentially
 morphosed. It is the only formation in exposed contact with the
 Peak stock and is about 5,000 feet thick.

#### CONTACT AUREOLE

c) rphic zones. On the south side of the aureole, where the Helena e may be traced into the contact aureole (Fig. 1), the first macrohange on approach to the granite contact occurs abruptly over by feet and is marked by the occurrence of light-colored diopside

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rocks. Tremolite rocks occur about 5 to 50 feet further from the granite contact than the diopside rocks but are commonly drab-colored and macroscopically indistinguishable from unmetamorphosed Helena dolo mite.

Within about 300 feet of the granite contact the rocks are coarsegrained, locally contain wollastonite and cordierite, and in places have



FIG. 1. Geologic map of the Granite Peak aureole.

been compositionally modified by reactions with magmatic solutions. Such reactions, many of which involved considerable bedding-plane replacement, mainly produced andraditic garnet, vesuvianite, calcite, epidote and quartz-bearing tactites similar to those in the contact aureole of the Marysville stock (Knopf, 1950).

In the following discussion, the tremolite rocks define the "transition zone", the diopside rocks, the "outer contact zone", and the wollastonite-cordierite rocks, the "inner contact zone". The metasomatically altered rocks of the inner contact zone are the subject of a separate study. Much

 [ABLE 1. MINERALS IN VARIOUS LAYERS FROM SOME SPECIMENS FROM THE TRANSITION

 AND OUTER CONTACT ZONE. ORIGINAL COMPOSITION INFERRED FROM MINERALS

 PRESENT AND THEIR RELATIVE ABUNDANCE. LISTED IN APPROXIMATE ORDER

 OF DECREASING DISTANCE FROM THE GRANITE CONTACT. MINERALS

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<sup>4</sup> Field number and approximate distance from mapped granite contact:

1. BH 1; 2000 (end of transition zone)

2. 44 m; 1500 3. 44 h; 1200

э.	44	п;	1200
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5. 12a2; 1100

6. 12a1; 1000

7.44 g; 1000

8. BH14; 900

9.44 k; 800

of the following discussion is based on the transition and outer contact zones, representative assemblages of which are listed in Table 1. The minerals were identified petrographically and by whole-rock *x*-ray diffraction study. Clinozoisite as used in Table 1 refers to a clinozoisitelike epidote group mineral. The structural state of the feldspars was not determined.

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TABLE 2. ESTIMATED RANGE IN COMPOSITION AND PRINCIPAL MINERALS IN WHICH CONSTITUENTS OCCUR IN THE UNMETAMORPHOSED HELENA DOLOMITE

Component	Estimated range (molar %)	Principal phases
SiO <sub>2</sub>	25–60	detrital quartz
CaO	10–40	calcite and dolomite
MgO	10–30	dolomite, chlorite and perhaps magnesian illite
Al <sub>2</sub> O <sub>3</sub>	less than 6	illite, chlorite, other mica group minerals <sup>1</sup>
K <sub>2</sub> O	less than 2	illite, detrital microcline
Na <sub>2</sub> O	less than 2	detrital plagioclase and perhaps mica group minerals
FeO	less than 1	dolomite and pyrite
Fe <sub>2</sub> O <sub>3</sub>	less than 0.1	detrital mica group minerals?

<sup>1</sup> Kaolinite and montmorillonite were not noted in the Helena dolomite.

# TABLE 3. MAGNESIUM AND CALCIUM CONTENT OF METAMORPHOSED AND UNMETAMORPHOSED HELENA ARGILLACEOUS BEDS

Starting	Weight		
aprennen no.	Mg()	CaO	- Mg/Ca-molar ratio
I	6.2	5.2	 1 7
2	8.3	0.0	1.7
3	4.8	0.0	
-1	10.7	9.1	1.6
5	6.2	4.7	1.8
7	1.8	6.0	1.8
•	9.2	8.4	1.5

Analyst: W. G. Melson

- 1. Unmetamorphosed argillaceous bed. Diffractometer trace shows chlorite and illite with small amount of calcite. Quartz is principal constituent. (field no. 44e3)
- 2. Unmetamorphosed argillaceous bed. Insoluble residue (10% HCl solution). (field no. 1pc.)
- 3. Unmetamorphosed interbedded carbonate-quartz and argillaceous beds. Homogenized sample. HCl insoluble residue. (field no. 76d)
- 4. Tremolite-quartz potassium feldspar-calcite hornfels. Beginning of outer contact zone. (field no. B111)
- Tremolite-quartz-plagioclase-phlogopite-calcite hornfels. Outer contact zone. (field no. 12a3)
- Tremolite-phlogopite-quartz clinozoisite-plagioclase hornfels. Outer contact zone. (field no. BH14)
- 7. Tremolite-phlogopite-quartz-clinozoisite hornfels. Outer contact zone. (field no. 44i3)

The three zones correspond generally to the "albite-epidote hornfels," "hornblende hornfels", and "pyroxene granulite" facies of Turner and Verhoogen (1960).

*Evidence of isochemical metamorphism.* Table 2 summarizes the ranges in composition of the Helena dolomite near the Granite Peak stock based on

(1) the amounts of insoluble residues and their mineralogy, (2) x-ray diffraction determinations of their dolomite-calcite ratios (Gulbrandsen, 1960), (3) calcium and magnesium contents (Table 3), and (4) an analysis given by Knopf (Table 4).

FABLE 4.	CHEMICAL	Composition	of a Doi	COMITE SPE	CIMEN OF	THE
	Hel	ena Formati	on (Knop	ч <b>г, 1963</b> )		

	Weight %	Mole %
SiO2	32.88	28.78
CaO	18.42	17.27
MgO	12.89	16.82
$Al_2O_3$	3.48	1.79
FeO	1.93	1.41
Fe <sub>2</sub> O <sub>a</sub>	0.16	0.06
NaO <sub>2</sub>	0.73	0.62
K <sub>2</sub> O	0,60	0.34
TiO <sub>2</sub>	0.14	0.09
MnO	0.10	0.07
$P_2O_5$	0.05	0.02
$CO_2$	27.71	30.37
$H_2O^+$	0.72	2.10
−O±H	0.09	0.26
	99.90	
	BaO, SrO, S, F not detected	

#### Analyst: E. H. Oslund

These data and the mineralogy of the hornfels indicate that metamorphism proceeded isochemically in the transition, outer and most of the inner contact zone except with regard to  $CO_2$  and  $H_2O$ . This necessitates karge volume changes of the hornfels due to loss of  $CO_2$  and  $H_2O$  perhaps on the order of those directly measured at Johnson Camp, Arizona (Cooper, 1957).

On the basis of the derived assemblages it is convenient to describe the composition of the Helena dolomite in terms of the system MgO-CaO- $KAlO_2-Al_2O_3$  with excess SiO<sub>2</sub>. This system can be graphically portrayed in a tetrahedron (Fig. 2) on which the dolomitic carbonate-quartz beds will be represented by the single join CaO-MgO with CaO-1/MgO-1, and

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the argillaceous beds will plot on the magnesian side of the join and slightly within the tetrahedron because of the abundance of mica group minerals and small amounts of carbonate. As indicated by the derived metamorphic assemblages (Table 1), many beds are of intermediate compositions.

# CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> System

The carbonate-quartz beds principally contain assemblages of the following six minerals: quartz, dolomite, calcite, tremolite, diopside and wollastonite. These assemblages are easily interpreted in terms of the system CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub>. Minerals characteristic of quartz-free



FIG. 2. Composition of Helena dolomite in terms of the system CaO-MgO-KAlO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> with excess quartz

carbonate assemblages, such as spurrite and monticellite, are not abundant in the Granite Peak aureole because of the abundance of quartz in the carbonate-quartz and argillaceous beds.

According to the phase rule a maximum of three of these six minerals may co-exist at equilibrium in the CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> system if temperature, total pressure, and chemical potentials of CO<sub>2</sub> and H<sub>2</sub>O are externally controlled, that is, if there are four independent variables (P=C+2-F=3, where C=5, F=4). These conditions are inherent assumptions in Goldschmidt's "mineralogical phase rule", and in Korzhinskii's classification of CO<sub>2</sub> and H<sub>2</sub>O as "perfectly mobile" components. In general the mineralogy of the carbonate-quartz beds in Table 1 is consistent with the thesis that H<sub>2</sub>O and CO<sub>2</sub> were perfectly mobile during metamorphism. However, four mineral assemblages in the CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> system occur in some hand specimens in two ways: (1) with three phases in individual layers, but with four in the specimen as a whole (*e.g.* No. 3 and No. 6, Table 1), and (2) as four phases in the same bed (*e.g.* No. 7, Table 1). The former case is characterized by reaction textures at layer interfaces (Figs. 3, 4).

Where four minerals co-exist in a five component system involving two volatile components, it is possible to write a devolatilization reaction between them (Korzhinskii, 1959). These reactions and their invariant point may be schematically portrayed as a function of two variables only by assuming all other variables constant. For two volatile systems, a plot of the reactions as a function of the composition of the co-existing volatile phase and temperature at fixed total volatile pressure is particularly useful in interpreting metamorphic assemblages. Figure 4 shows such a plot for the reactions which occurred in the carbonate-quartz beds. The excess of quartz allows plotting of the assemblages on the single join, CaO-MgO.

The reaction of calcite and quartz to wollastonite is the only reaction noted in the aureole for which two-volatile experimental data are available at present (Greenwood, 1962). Although of particular interest in this and many other metamorphic terrains, experimental studies of the remaining reactions are lacking. These reactions are shown schematically in Fig. 3 on data from the Granite Peak aureole and on the basis of the  $CO_2$  and  $H_2O$  evolved or added to the reactants (Greenwood, 1962).

Significance of initial water content. On the basis of field and petrographic features diopside was formed by two reactions at the beginning of the outer contact zone. Some dolomitic carbonate-quartz beds reacted directly to diopside (reaction 2, Fig. 5) although most reacted to diopside after the intermediate formation of tremolite (reaction 1, Fig. 6).

These two different paths are evidently related to the initial volatile content of the rocks. Where the H<sub>2</sub>O content presumably was relatively low, dolomite and quartz reacted directly to diopside. For higher H<sub>2</sub>O contents, tremolite formed. These two reaction paths may be related to volatile composition at constant total volatile pressure by Fig. 5. Alternatively, they may be shown in a more generalized manner on a  $CO_2$ -H<sub>2</sub>O chemical potential plot at constant temperature and pressure (Fig. 6) as advocated by Korzhinskii (1959).

Tale is common in the low temperature portion of contact aureoles in impure carbonate rocks (Cooper, 1957; Tilley, 1948). Although searched for specifically, tale was not noted in the transition zone of the Granite Peak aureole. The absence of tale is perhaps also related to the initial



FIG. 3. Layered hornfels, outer contact zone. Dark layers are mainly quartz, tremolite, and phlogopitic biotite; light layers, diopside, quartz and calcite. Note expansion of diopside-rich reaction layer into quartz-tremolite-biotite layer on lower left hand side of specimen. Actual size, Southeast side of Granite Peak.

Sketch shows dense reaction zone of diopside between layers. Large embayed relict quartz grains in diopside-rich layer. Diopside shown by high relief; tremolite, elongate crystals; phlogopitic biotite, stippled; pyrite, opaque. Clinozoisite and plagioclase occur in both layers.

volatile content of the rocks. Intragranular fluids of the Helena dolomite were presumably low in H<sub>2</sub>O, thus preventing the formation of talc.

The isothermal co-existence of the assemblages tremolite-calcite-quartz and dolomite-quartz requires volatile compositional gradients at their



FIG. 4. Layered hornfels. Dark layers principally tremolite, quartz, calcite, and phlogopitic biotite; light layers are diopside, quartz and calcite. Note concentration of phlogopitic biotite in some areas at contact of layers. Outer contact zone, southeast side of Granite Peak. Actual size.

CEAK, ACUAL SIZE. Sketch shows details at a layer contact. Diopside, high relief; tremolite, elongate crystals; phlogopitic biotite, stippled. Matrix mainly quartz. contacts. Figure 5 clearly shows this. If  $CO_2$  and  $H_2O$  were homogenized between such layers, only one of these assemblages would be stable unless volatile composition coincided with the reaction curve (1, Fig. 5). It is thus likely that on an outcrop and even hand specimen scale original



in the carbonate-quartz beds.

differences in volatile contents created compositional gradients in the lower metamorphic grades.

The contact between such assemblages may be regarded as an isograd produced by pore fluid compositions rather than temperature. The existence of such isothermal isograds was predicted by Greenwood (1962) on theoretical grounds. In this regard, it is interesting that such features occur only in the transition and beginning of the outer contact zone, that is, in the low temperature portion of the aureole. In the terms proposed by Zen (1963),  $CO_2$  and  $H_2O$ , although "boundary value" components on an individual bed scale, behaved as "initial value" components on a hand specimen or outcrop scale in the low temperature portion of the aureole. The "perfect mobility" of  $CO_2$  and  $H_2O$ 



FIG. 6. CO<sub>2</sub>-H<sub>2</sub>O chemical potential diagram for reactions in the carbonate-quartz beds.

at higher temperatures in the aureole is schematically shown by the convergence of the two paths of metamorphism shown in Figure 6.

Four phases in the CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> system in a single bed, all in mutual contact, such as in specimen No. 7, Table 1, requires internally buffered CO<sub>2</sub> and H<sub>2</sub>O fugacites, or disequilibrium if CO<sub>2</sub> and H<sub>2</sub>O are assumed to have been "perfectly mobile." The latter is unlikely in view of the evidence just presented and in the textural equilibrium of the minerals.



FIG. 7. Hornfels, outer contact zone. White layers mainly diopside, quartz, and calcite

Sketch shows detail along fracture. Diopside indicated by high relief; tremolite in

Gray layers mainly tremolite and quartz. Tremolite, calcite, and quartz have reacted in

form diopside along fracture. Actual size. Southeast side of Granite Peak.

CENTER OF FRACTURE

elongate crystals. Quartz and calcite in matrix,

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Significance of initial CaO-MgO ratio. As shown by Table 3, argillaceous beds may contain CaO-MgO ratios of less than one. Such beds, after metamorphism, may contain tremolite without calcite. Where such beds are in contact with carbonate-quartz beds (diopside-calcite beds) in the inner part of the outer contact zone, reaction 3 (Fig. 6) occurs (Figs. 3, 4, 7). However, because of the low diffusion rates of "inert" components, this incompatibility is commonly preserved. Diffusion was, however, sufficiently rapid along fractures (Fig. 7) to allow rapid equilibration of the assemblages.

Where reaction (3) occurred at layer interfaces, the composition of the pore fluids may have been maintained in the entire specimen at a molar ratio of  $CO_2/H_2O = 3/1$ . This is the ratio at which reaction (3) proceeds at a maximum temperature for a given total pressure of volatiles (Fig. 5; also Greenwood, 1962). Such buffering may continue until either calcite or tremolite is completely eliminated. This last process will be strongly controlled by the diffusion rate of CaO (Fig. 7).

## CaO-MgO-KAlO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O System

The application of the phase rule to the argillaceous beds is complicated by the larger number of constituents involved and resulting uncertainties in assessing the behavior of components. Some simplifications nonetheless allow graphical portrayal of most of the assemblages by a tetrahedron.

Components which may be neglected occur in a single phase and are not involved in "discontinuous" reactions, that is, reactions which produce new phases at the expense of others on approach to the granite contact.  $TiO_2$ (sphene),  $FeS_2$  (pyrite) and  $Na_2O$  (plagioclase, or rarely scapolite) are three such components.

Components which are present in such small amounts that they apparently do not give additional phases but rather substitute isomorphously for major components may also be neglected in qualitative interpretations. For example, FeO and MnO, which are present in small amounts (Table 2), probably substitute for MgO. Similarly, any small amount of  $Fe_2O_3$  present initially substitutes mainly for  $Al_2O_3$  in the epidote minerals or in cordierite.

In view of this simplification, reactions in the argillaceous beds may be reduced to the CaO-MgO-KAlO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O system. The component KAlO<sub>2</sub> is preferred rather than  $K_2O$  because reactions involving phlogopitic biotite and potassium feldspar involve transfer of  $K_2O$  and Al<sub>2</sub>O<sub>3</sub> as the single component KAlO<sub>2</sub>.

It is now possible to portray the assemblages of the argillaceous beds, and aureole as a whole, in terms of a tetrahedron.  $SiO_2$  need not be plotted as a separate component because of its presence in excess.

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Similarly,  $CO_2$  and  $H_2O$ , where they are "perfectly mobile", do not give rise to additional phases. Thus, the assemblages may be expressed in terms of the CaO-MgO-KAlO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system with excess quartz.

On this tetrahedron (Fig. 2), the assemblages derived from the  $c_{af}$  bonate-quartz beds reduce to the single join CaO-MgO. The treatment of the non-volatile components as a whole is given in Table 5 in terms defined by Korzhinskii (1959).

Figure 8 summarizes the development of the aureole in terms of this tetrahedron and the reactions relating one tetrahedron to another. These reactions are based mainly on petrographic data. In the transition zone, the reactions in argillaceous beds are particularly difficult to infer because various original mica group minerals were involved. "Illite" as used in Fig. 8 applies to a hypothetical mean composition of the mica group

 TABLE 5. TREATMENT OF COMPONENTS. DESIGNATION OF COMPONENTS

 Follows Terms Defined by Korzhinskii (1959)

Determining "inert" components (	'ao Mgo ko Mo
Excess component	$\operatorname{SiO}_2$ SiO <sub>2</sub>
Accessory (indifferent) components	TiO <sub>2</sub> , Na <sub>2</sub> O, S <sub>2</sub>
Isomorphous components	FeO, Fe <sub>2</sub> O <sub>3</sub> , MnO

minerals in a given bed. Thus, reactions 5 and 6 are particularly schematic.

Assemblages in the transition and outer contact zones were determined evidently by composition and pressures of pore fluids as well as temperature and thus alternative assemblages are shown in Fig. 8.

The five phase assemblage potassium feldspar, quartz, diopside, tremolite, and phlogopite occurs in some assemblages in the outer contact zone (Table 1, nos. 3, 8). This assemblage suggests disequilibrium if the above treatment of components is correct, that is, if there was not an additional determining "inert" component to the four listed in Table 5. However, this assemblage does not indicate that the beds were partially closed to volatiles because potassium feldspar, quartz, diopside, tremolite and phlogopite include both the reactants and products of a solid-solid reaction (no. 7, Fig. 8). The problem as to whether this assemblage reflects disequilibrium or the effect of an additional component may be resolved in part by determinations of the mineral compositions. This is presently being attempted by means of electron microprobe analyses as part of a general study of component partitioning in the contact aureole.

The validity of Fig. 8 in portraying the actual evolution of metamorphic assemblages in the Granite Peak aureole is subject to two important amitations. First, a total of but 40 specimens were examined in detail. Even a single new assemblage may modify joins shown in a single CaO- $Mg(0-KAIO_2-AI_2O_3)$  tetrahedron. This is particularly true for assemblages in the inner contact zone. As shown by the reorientation of most planes



FIG. 8. Summary of development of assemblages in terms of the CaO-MgO-KAIO<sub>2</sub> Al<sub>2</sub>O<sub>4</sub>-CO<sub>2</sub> H<sub>2</sub>O system with excess quartz.

within the tetrahedron on passage from the outer to inner contact zone, many other reactions in addition to 9 were involved. In the specimens at hand there is little direct textural evidence for these reactions.

The second limitation to Fig. 8 is in the restricted compositional range of the Helena dolomite. Only stability relations in volumes of the tetrahedron which are near the CaO-MgO join may be inferred from the hornfels. For example, little information was obtained from the hornfels for the behavior in the ternary KAlO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO with excess silica.

## EXTERNALLY CONTROLLED VARIABLES

*Lithostatic pressure.* The amount of lithostatic pressure at the time of intrusion of the Granite Peak stock is uncertain but limits may be established. The principal source of uncertainty is in the estimate of the amount of erosion which occurred between the end of Mesozoic deposition and the time of intrusion of the Granite Peak stock (Melson, 1966).

About 20,000 to 30,000 feet of sedimentary rocks were above the Helena formation at the end of Mesozoic deposition and about at the time of late Cretaceous folding and faulting, or "Laramide orogeny." The Granite Peak stock was emplaced after folding and evidently at about the same time as the Boulder batholith. It is difficult to place a lower limit on the amount of cover at the time of intrusion although a maximum limit is about 2.5 kilobars assuming a mean rock density of 2.7 gms/cc. Inasmuch as considerable erosion occurred between folding and intrusion, and on the basis of considerations presented by Barrell (1907) for the Marysville stock, a value of about 1 kilobar was probably attained at the present level of exposure.

*Volatile pressure.* During metamorphism large quantities of CO<sub>2</sub>-rich volatiles were evolved producing volume changes between 20 to 30 per cent in the initially dolomitic carbonate-quartz beds. Fluid inclusions in quartz veinlets and diopside crystals require the presence of a fluid phase during their formation and suggest that volatile pressure equalled total pressure for at least part of the time.

If, in response to rapid increase in temperature, volatiles were evolved rapidiy, volatile pressure may have exceeded the value of initial load pressure for a short time, particularly in rocks of low permeability. Irregular breccia bodies and dikes composed of hornfels occur in places and perhaps formed when volatile pressure exceeded the strength of the rocks.

Fractures which show evidence that volatiles moved along them are locally abundant. In areas where such fractures gave access to the surface, the volatile pressure may have been slightly less than load pressure.

The aureole thus contains features which suggest that total volatile pressure varied from equal to initial load pressure plus the strength of the rocks, to perhaps less than load pressure.

*Temperature distribution*. The temperature at the granite contact may be inferred from experimental work on the granite solidus (Tuttle and Bowen, 1958). The composition of much of the stock, as indicated by

modal analyses, falls near the granite minimum at water pressures on the order of one to a few kilobars and is similar to that of the Quincy and Westerly granites which have experimentally determined melting tem-

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Most of the reactions which occurred in the aureole evolved a  $CO_2$ -rich huid. On the other hand, the abundant biotite and hornblende of the granite, and local abundance of chlorites in the hornfels at the granite

TABLE 6. APPROXIMATE TEMPERATURES AT WHICH REACTIONS IN THE
CaO-MgO-SjO <sub>2</sub> -CO <sub>2</sub> -H <sub>2</sub> O System Occurred in the
GRANITE PEAK AUREOLE

Reaction Number	Approximate	Facies and temperature range
(Fig. 4)	temperature (C)	(Turner and Verhoogen, 1960)
1	350-400	albite-epidote hornfels 430
2	-400	hornblende hornfels 500–665
3	-400-500	hornblende hornfels 500–665
4	-650-700	pyroxene granulite 700

contact suggest  $H_2O$  was an abundant constituent in the granite. It is thus likely that gradients in pore fluid composition occurred across the inner contact zone even though total volatile pressure may have been maintained at around 1 kilobar.

The lack of chilled contacts and the abundant evidence of emplacement of the stock by magmatic stoping (Melson, 1966) indicate that the stock was active over a considerable period of time. Aided by increased rock conductivity as a result of the movement of volatiles from the aureole, the aureole thus may have approached a steady state temperature gradient.

On the basis of stability relations calculated by Weeks (1956) for the reaction of dolomite and quartz to diopside, a temperature of 400° C. for a CO<sub>2</sub> pressure of 1 kilobar existed at a minimum of 700 feet from the granite contact where this reaction evidently occurred. Thus, if the temperature at the contact was about 700° C., the temperature gradient was on the order of  $0.5^{\circ}$  C. per foot.

Table 6 gives the approximate temperatures at which some of the reac-

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tions occurred based on distances from the granite contact and the above assumptions of the temperature gradient. These temperatures correspond approximately to estimates for the albite-epidote hornfels, hornblende. hornfels and pyroxene granulite facies of Turner and Verhoogen (1960).

Because some reactions evidently occurred at different distances from the Granite contact, particularly in the transition and outer contact zones, they probably proceeded or began over a temperature interval Based on the evidence of the previous sections, this interval and the reaction which occurred were related to the initial volatile content of the beds and interactions between layers of contrasting compositions.

#### CONCLUSIONS

Mineral assemblages in the Granite Peak aureole were determined primarily by temperature, externally controlled volatile pressures, and the initial content of non-volatile constituents in the Helena dolomite. However, in the lower temperature portion of the aureole, the reaction which occurred at a given temperature was evidently also related to the initial volatile content, particularly of H<sub>2</sub>O. Thus, contrasting assemblages, some of which are thought to represent different facies and temperatures in present classifications, co-exist in the same hand specimen or outcrop.

The textures and co-existence of such assemblages suggest that CO: and H<sub>2</sub>O may not be regarded a priori as "perfectly mobile" or "boundary value" components during metamorphism, particularly in the lower metamorphic grades. Disequilibrium in response, for example, to slow reaction rates is an alternative explanation of the isothermal co-existence of such assemblages. However, textural features and application of the phase rule to individual beds suggest that this co-existence is not a result of disequilibrium.

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#### REFERENCES

BARRELL, J. (1907) Geology of the Marysville mining district, Montana, U.S. Geol. Survey Prof. Paper 57.

COPER, J. R. (1957) Metamorphism and volume losses in carbonate rocks near Johnson

Camp, Cochise County, Arizona. Geol. Soc. Am. Bull. 68, 577-610. GREENWOOD, H. J. (1962) Metamorphic reactions involving two-volatile components.

Ann. Rept. Director, Geophys. Lab. 82-85. GELBRANDSEN, R. A. (1960) A method of x-ray analysis for determining the ratio of calcite to dolomite in mineral mixtures. U.S. Geol. Survey Bull. 111-D, 147-152.

HARKER, A. AND O. F. TUTTLE (1956) Stability of wollastonite. Am. Jour. Sci. 251, 239. SOPF, A. (1913) Ore deposits of the Helena mining region, Montana: U.S. Geol Survey

(1950) Marysville granodiorite stock. Am. Mineral. 35, 834–844. (1957) Boulder bathylith of Montana. Am. Jour. Sci. 255, 81–103.

---- (1963) Geology of the northern part of the Boulder bathylith and adjacent area,

Montana. U.S. Geol Survey, Misc. Geol. Investig. Map 1-381,

KORZHINSKII, D. S. (1959) Physicochemical basis of the analysis of the paragenesis of minerals. Transl. by Consultant Bureau, Inc., N.Y.

MELSON, W. G. (1966) Geology of the Lincoln area, Lewis and Clark County, Montana:

PARDEE, J. T. AND F. C. SCHRADER (1933) Metalliferous deposits of the greater Helena

mining region, Montana. U.S. Geol. Survey Bull. 842. HLLEY, C. E. (1948) Earlier stages in the metamorphism of siliceous dolomites. Mineral.

TURNER, F. J. AND J. VERHOOGEN (1960) Igenous and Metamorphic Petrology. McGraw-

TUTTLE, O. F. AND N. L. BOWEN (1958) Origin of granite in the light of experimental studies in the NAISi<sub>2</sub>O<sub>8</sub>-KAISi<sub>2</sub>O<sub>8</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system: Geol. Soc. Am. Mem. 74.

WEEKS, W. F. (1956) A thermochemical study of equilibrium relations during metamorphism of siliccous carbonate rocks. Jour. Geol. 61, 259-261.

WEILL, D. F. AND W. S. FEISS (1964) A discussion of the Korzhinskii and Thompson treatment of thermodynamic equilibrium in open systems. Geochim. Cosmochim. Acta, 28,

ZEN, E-AN (1963) Components, phases, and criteria of chemical equilibrium in rocks. Am. Jour. Sci. 261, 929-942.

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