

COMPOSITION AND CRYSTALLIZATION OF MAFIC
MINERALS IN THE GUADALUPE IGNEOUS
COMPLEX, CALIFORNIA

MYRON G. BEST, *Department of Geology,
Brigham Young University,
Provo, Utah*

with chemical analyses by

EDWARD L. P. MERCY, *Grant Institute of Geology,
University of Edinburgh,
Edinburgh, Scotland.*

ABSTRACT

Chemical analyses of twenty coexisting pyroxenes, hornblendes, biotites, and ilmenites have been made from the Guadalupe igneous complex—a differentiated gabbroic intrusion which crystallized under a relatively high f_{H_2O} . The differentiates are similar in mineralogy and bulk chemical composition to the common calc-alkaline plutonic suite of orogenic regions.

Special attention has been devoted to the coexisting Ca-rich clinopyroxene and orthopyroxene which characterize the early gabbroic differentiates. These pyroxenes have extreme, and very uniform, contents of Ca, and this fact, together with comparisons of their Mg-Fe partition with pyroxenes from other types of rocks, suggest those from the Guadalupe crystallized at relatively low temperatures, such that the liquidus was depressed far down on the pyroxene solvus. Crystallization of pigeonite (Ca-poor clinopyroxene) was precluded under these conditions. This trend of pyroxene crystallization, the first of its kind to be established, is considerably different from the Skaergaard trend and is closely similar to variations found in pyroxenes from granulite-facies metamorphic rocks.

Hornblende appears as a primary phase early in the differentiation sequence and biotite appears in the more Fe-rich gabbroic rocks. With decreasing temperature, and possibly increasing f_{H_2O} , hornblende and biotite take the place of pyroxenes in the intermediate differentiates, diorite and quartz monzonite. Biotite is the sole ferromagnesian silicate in the late silicic differentiates, granite and granophyre. Hornblende and biotite from successive differentiates show enrichment in Fe relative to Mg, but variations in concentrations of elements are not nearly as regular as the variations in pyroxenes, possibly because of the range in rock types represented.

Coexisting orthopyroxene, clinopyroxene, hornblende, and biotite, in that order, have decreasing concentrations of Fe^{2+} and Mn but increasing Al and Ti.

The dominant oxide phase in gabbroic rocks is ilmenite, whereas intergrowths of magnetite-ilmenite occur in more silicic differentiates. Pyrite and pyrrhotite appear sparingly in the earliest gabbroic rocks. The ilmenites contain only about seven atomic percent hematite in solid solution, indicating f_{O_2} was about 10^{-10} to 10^{-13} bars at crystallization temperatures (inferred to be approximately 1100° to $900^\circ C$) and remained at values low enough during cooling to prevent extensive oxidation. The f_{O_2} is only slightly lower than that inferred for the crystallizing Skaergaard magma. Utilizing simplifying assumptions, it is shown that the Guadalupe magma, though having a relatively high f_{H_2O} , could have maintained a low f_{O_2} if other "volatiles," such as S_2 , SO_2 , CO_2 , etc., were present.

High f_{H_2O} and early crystallization of hornblende play an important role in the develop-

ment of the calc-alkaline trend from basaltic magmas. Relatively high f_{O_2} is not a necessary accompanying factor. In fact, high f_{O_2} alone cannot produce the characteristic hydrous ferromagnesian silicates of this trend. It has yet to be demonstrated whether relatively high f_{O_2} is a pertinent factor in the evolution of natural magmatic sequences.

INTRODUCTION

Many studies of pyroxenes from mafic intrusive rocks have been made over the past fifteen years in an effort to establish compositional trends relative to magma type. Thus Murray (1954), Wilkinson (1956), and Boesen (1964) have demonstrated that in alkalic basaltic magmas only one pyroxene crystallizes, it being a very calcic clinopyroxene with little Fe-enrichment, lacking exsolution lamellae, and commonly showing marginal compositional zoning. Pyroxenes from the more common, usually tholeiitic, magma types have been investigated by Hess (1949), Brown (1957), Brown and Vincent (1963), Carmichael (1960), and McDougall (1961). In such intrusive magmas, two pyroxenes, a Ca-rich clinopyroxene and a Ca-poor phase, both exhibiting exsolution lamellae, crystallize together in the early and middle stages of differentiation. In the latter more Fe-rich stages, only a Ca-rich phase crystallizes. The Ca-poor pyroxene is an orthopyroxene in the early stages of differentiation but in the middle stages a monoclinic pigeonite crystallizes, which may subsequently invert to orthopyroxene.

During an investigation of the Guadalupe igneous complex in the western Sierra Nevada foothills (Best, 1963) petrographic examination of the pyroxenes in the gabbroic differentiates disclosed unusual compositional features. The magma from which the complex formed crystallized at relatively high water fugacities, f_{H_2O} , indicated by the abundance of hornblende and biotite in the more Fe-rich gabbroic rocks and the presence of these phases to the exclusion of pyroxenes in the more silicic differentiates.

Nineteen new chemical analyses are presented in this paper, defining (1) a new trend of pyroxene crystallization in "wet" mafic magmas which are undergoing differentiation, (2) the nature of Fe-Mg-Ti phases in differentiates of such a magma, (3) the partition of elements between the crystallizing phases, and (4) the f_{H_2O} and f_{O_2} at which crystallization occurred. From the data, inferences are made on the evolution of the calc-alkaline plutonic suite in general, of which the Guadalupe seems to be an example.

Collection sites of samples from which minerals were separated and analyzed (see Table 1) are shown in Figure 1.

FIELD RELATIONS AND PETROGRAPHY

The Guadalupe complex is a late Jurassic, mesozonal, partially concordant intrusion of about sixty square miles areal extent surrounded by

massive to strongly foliated metasedimentary and metavolcanic rocks of the greenschist facies. Contact metamorphism accompanying crystallization of the complex extends as much as a mile outward from the exposed contact adjacent to micaceous rocks; mineral assemblages near the contact indicate recrystallization under conditions of high water pressure, transitional between the hornblende hornfels and the almandine-amphib-

TABLE 1. PETROGRAPHY OF ROCKS FROM WHICH MINERALS WERE SEPARATED AND ANALYZED

Sample	140 ¹	128	132 ¹	153 ¹	83	106	154	148
Rock type	Gabbroic rocks						Quartz monzonite	Granite
Grain size (average in mm)	3	0.3	0.3	1	0.3	1	0.5	0.5
Mode ⁶								
plagioclase	69.8	56	57	55.2	65.5	63	28	16
clinopyroxene	26.5 ²	28 ²	27 ²	12.6 ²	18.6 ²	16	0	0
orthopyroxene	2.6 ²	3 ²	4 ²	1.5 ²	1.0	11 ²	0	0
ilmenite	0.5 ²	2 ²	4 ²	1.7 ²	5.5	7	} trace	<1
magnetite	0.0	trace	0	0.0	0.0	0		
pyrite	0.1 ³	0	0	0.0	0.0	0	0	0
pyrrhotite	0.1 ³	0	0	0.0	0.0	0	0	0
hornblende	0.0	11 ²	8 ²	10.8 ²	3.6	2	4 ²	0
biotite	0.0	0	0	4.8 ²	3.3	0	4 ²	3 ²
quartz	0.0	0	0	5.8	2.5	0	24	32
K-feldspar	0.0	0	0	7.6	0.0	0	40 ⁴	48 ⁵
other	0.4	0	<1	<0.1	<0.1	1	0	<1
% An in plagioclase	71-82	52-58	45-57	23-52	28-55	43-54	9-20	13-24

¹ 140 was collected from the same outcrop as 101, 132 as 105, and 153 as 113. In each case the rock with the smaller number is described, together with samples 83 and 106, in the earlier paper (Best, 1963). Analyses of rocks 101, 113, and 83 are presented therein. Modes listed are for the earlier, analyzed rock samples.

² Minerals chemically analyzed and referred to in Tables 3 through 9, where they are identified by the appropriate rock number with a suffix added: o for orthopyroxene, c for clinopyroxene, h for hornblende, b for biotite, and i for ilmenite.

³ Proportion of types of opaque minerals visually estimated; total opaque mode determined by point counter.

⁴ Perthitic microcline.

⁵ Perthite.

⁶ Volume percent based on approximately 1500 points.

olite facies. Rock types in the complex range from troctolite to granophyre. Gabbroic rocks, encompassing (mainly for convenience of discussion) rocks consisting of pyroxene and plagioclase with variable, and sometimes substantial, proportions of olivine, hornblende, and biotite are exposed in the southwest portion of the complex. A small central portion of the complex is underlain by diorite, and to the east is an arcuate area of agmatite. Small hills in the region of diorite are capped by quartz monzonite; more voluminous quantities of silicic rock occur as the matrix

of the agmatite¹ and as a granite and granophyric granite sheet overlying the agmatite. Most boundaries between these recognized rock types are gradational. The complex appears, from several lines of evidence (Best, 1963, p. 245-250), to have developed essentially, in its broader aspects, by differentiation of a mass of basaltic magma, collapse and fragmenta-

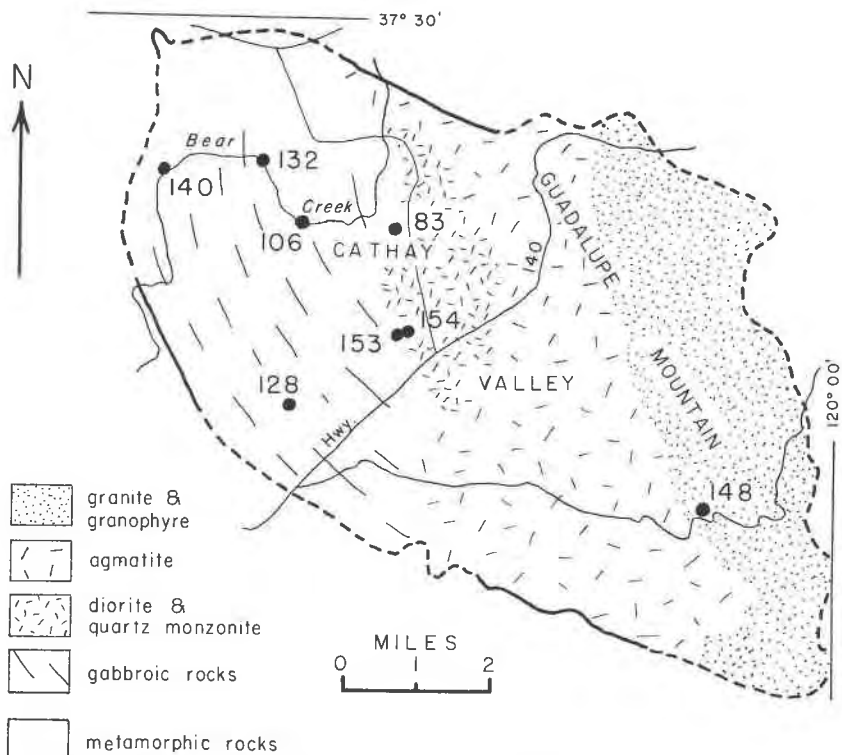


FIG. 1. Generalized geologic map of the Guadalupe igneous complex, located astride Highway 140 between Merced and Mariposa in the Sierra Nevada foothills, California. Rock samples from which constituent minerals were analyzed were collected at the numbered localities.

tion of the roof into the residual silicic magma (forming agmatite) and accumulation of granite in the upper portions of the original chamber. In detail, however, there may have been modifications or additions to the main magma during differentiation because of, for example, changes in the cryptic variation in gabbroic rocks (Best, 1963, p. 237) and the rather abrupt transition from diorite to quartz monzonite in the central part of

¹ Blocks of mafic rock in leucocratic matrix.

the complex. Cryptic mineral variations are less pronounced in the middle gabbros than in gabbroic rocks to the west and to the east.

Many of the structures observed in the Guadalupe gabbroic rocks are similar to those described and illustrated by Miller (1938). Along the eastern part of the gabbroic area, and locally elsewhere, features akin to those in his Plate 2 have been found, together with small subtle lenticular layers whose definition, as Miller notes for the San Marcos gabbro, is mainly produced by variations in texture and grain-size. Large scale and seemingly more continuous layering characterize the gabbroic mass as a whole; these layers, a few feet to several tens of feet wide, and apparently concordant to the steep western contact of the complex, are displayed as long belts of exposed rock, with only subtle variations in texture, mode, and grain-size evident between belts. Local nodular-structured gabbroic rock is related to the presence of large (up to several centimeters in diameter) poikilitic hornblende grains. Just below sample locality 132 in Bear Creek is a zone about 200 feet wide and parallel to the layering on either side, consisting of lenses of hornblende-rich melanocratic, fine-grained gabbroic rock enclosed in more leucocratic and coarser-grained, hornblende-free gabbro. Igneous lamination is strongly developed in the coarse gabbroic rocks along the western margin of the complex, but elsewhere only locally and to lesser degrees.

The brief observations of structures in the Guadalupe gabbroic rocks (see also descriptions in Best, 1963¹) might be explained by local, intermittent movement of magma bringing together crystal mushes of differing grain-size and mode coupled with more quiescent crystallization. The zone of auto-injection exposed in Bear Creek may reflect a major disturbance along the walls of the magma chamber; fine, hornblende-rich portions at the top were transferred to lower depths of the chamber and there included in less hydrous magma. Alternatively, this zone and coincident discontinuities in cryptic mineral variations may reflect a new influx of magma, which mixed with the residual magma already present, and in so doing disturbed the previously accumulated crystal mush along the walls of the magma chamber. Similar but better evidence for multiple influx of magma in a differentiating intrusion is presented by Deer and Abbott (1965) for a gabbroic complex in east Greenland.

Petrographic notes on the principal rock types can be found in the earlier paper (Best, 1963). In order to convey an idea of the petrography of the rocks from which mineral analyses were made, some pertinent data

¹ Paleomagnetic data obtained by S. Grommé are compatible with interpreted structural relations stated in Best (1963). The data are to be published soon in the *J. of Geophys. Res.*

are quoted in Table 1, and photomicrographs are shown as Figures 2 to 6. Note that, although the early Fe-poor and the late Fe-rich gabbroic rocks have typical igneous textures, the middle gabbros (represented by 128 and 132) do not. Pyroxenes and the hornblendes molded around them or occurring independently are anhedral to subhedral; plagioclase grains are anhedral and show less complex twinning and less pronounced zoning

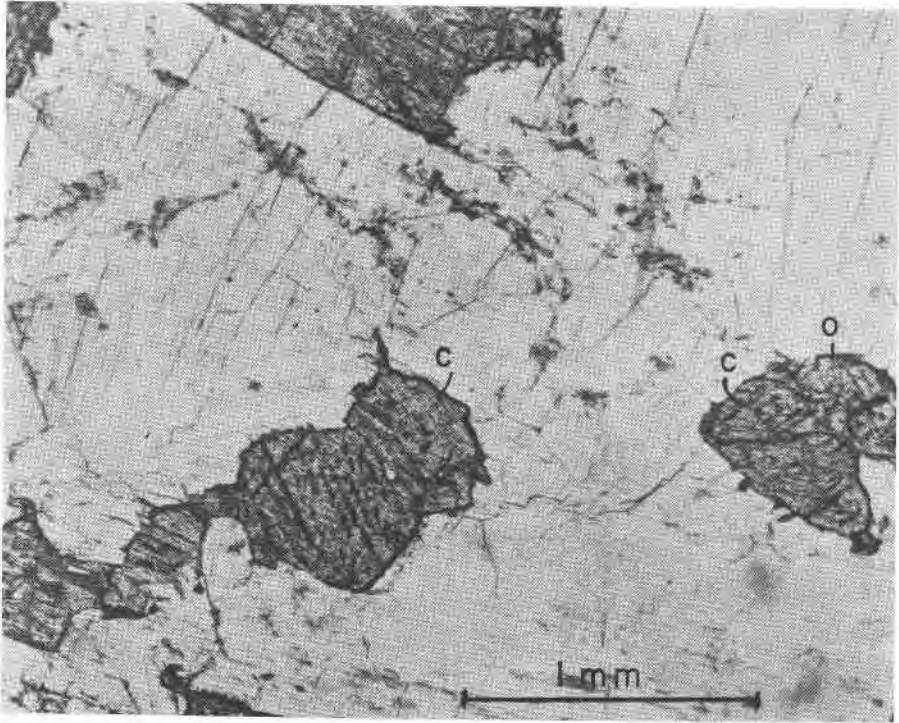


FIG. 2. Sample 140. Plagioclase, clinopyroxene, and orthopyroxene.

than do the more typically igneous appearing gabbroic rocks which crystallized before and after. In fact, the textures of many middle gabbros are strongly reminiscent of those found in hornblende—two pyroxene granulites, such as from Broken Hill, Australia (see Binns, 1964). The possibility exists, then, of autometamorphism of the middle gabbros, perhaps facilitated by slow cooling in the presence of an intergranular aqueous phase.

Additional comment on the opaque minerals in the Guadalupe rocks is in order here because of the meager information given in the earlier paper. The Fe-poor gabbroic rocks, such as 140, exposed within a mile

of the western contact of the complex contain pyrrhotite and pyrite, either as independent anhedra or together in composite grains lacking any planar faces. Ilmenite occurs very sparingly along margins of silicate grains. Local specks and patches of ilmenite and minor magnetite within olivines and pyroxenes seem related to post-crystallization exsolution. The middle gabbroic rocks, represented by 128 and 132, contain ilmenite

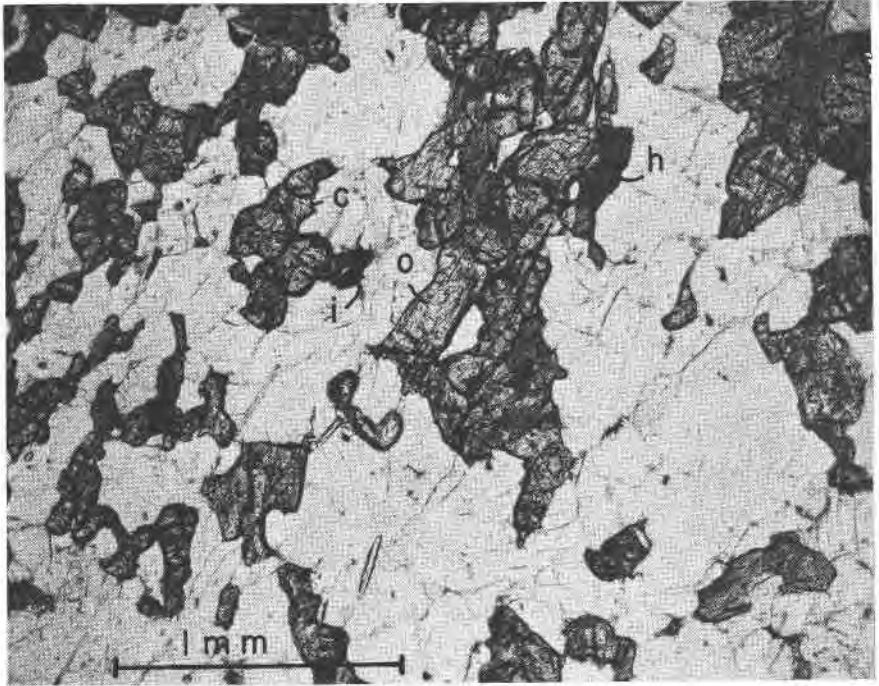


FIG. 3. Sample 128. Plagioclase, clinopyroxene, orthopyroxene, hornblende, and local apatite and ilmenite.

as the dominant opaque mineral. The grains are equant to elongate, some consisting of more than one crystal, and seem randomly distributed throughout the rock. It appears as though they precipitated from the magma simultaneously with the silicates. Magnetite with lamellae of ilmenite is locally conspicuous in many samples (S. Grommé, personal communication, 1966). Ilmenite is the sole opaque phase in 153, typifying the Fe-rich gabbros, and occurs as very irregularly shaped grains, only a few of which approximate a platy or skeletal outline. In quartz monzonite 154, numerous small grains of ilmenite occur together with less common aggregated clusters of larger ilmenite and magnetite. Triangular-

textured (111) lamellae of ilmenite locally border the magnetite. The clusters are reminiscent of the clustered oxides shown by Vincent and Phillips (1954, Plate IA) in Skaergaard gabbros. The oxide mineral in granite 148 is magnetite with coarse lamellae of ilmenite.

In summarizing the observations on opaque minerals in the Guadalupe rocks it is worthwhile to emphasize that the sulfides only occur in the

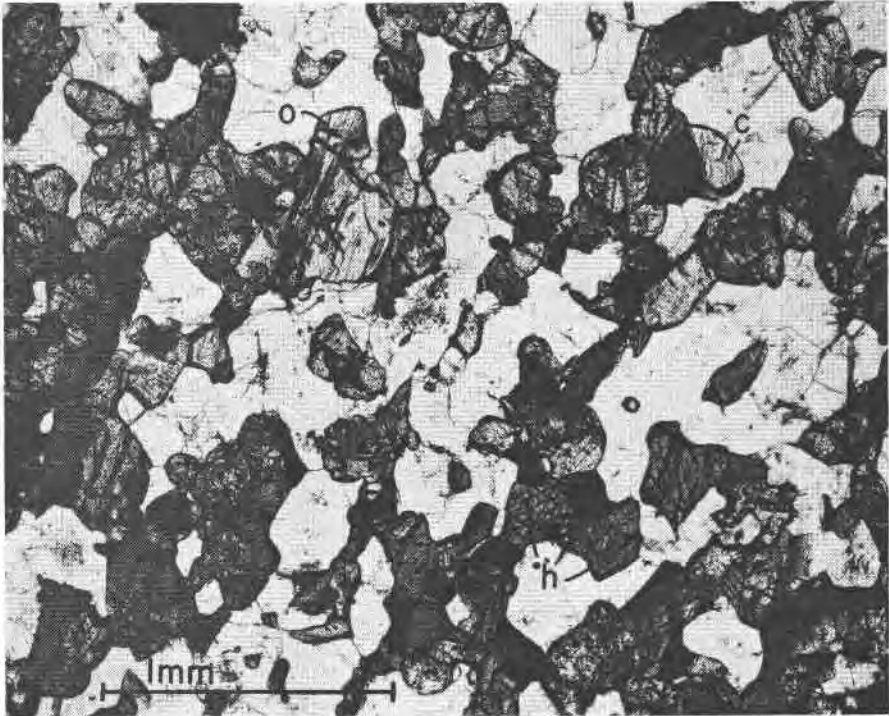


FIG. 4. Sample 132. Plagioclase, hornblende, clinopyroxene, orthopyroxene, and ilmenite.

early gabbroic rocks. In the Skaergaard intrusion, by comparison, Cu-sulfides first appear in the main body of layered gabbro; pyrrhotite, pyrite, and minor chalcopyrite occur in the late Fe-, Si-rich differentiates (Wager, et al, 1957).

Thorough studies of Fe-Ti oxides in igneous rock suites similar to the Guadalupe complex are seriously needed.

PREPARATION OF SAMPLES

Rock samples were crushed, sized, washed free of very fine particles, and run repeatedly through a magnetic separator and heavy liquids

(methylene iodide and Clerici's solution) to obtain the desired concentrate. In addition, the pyroxene concentrates from rocks 128 and 153 were washed for fifteen minutes in warm, moderately concentrated HCl in an attempt to remove partial films of yellow-brown ferric oxide adhering to the grains. This procedure was successful with 128 but only partly so with 153.

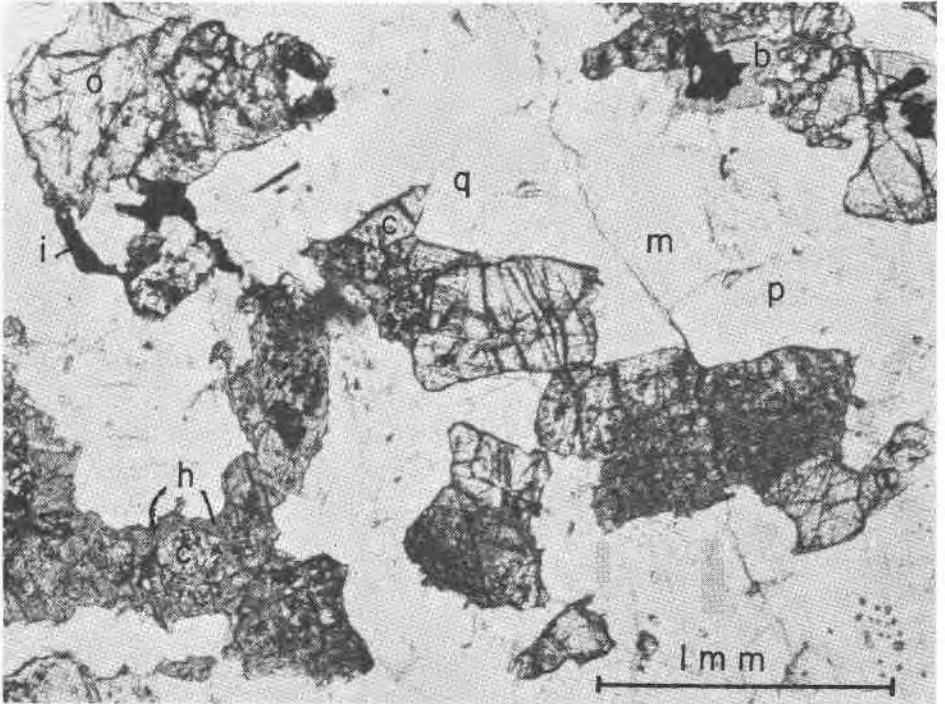


FIG. 5. Sample 153. Plagioclase, interstitial microcline, and quartz constitute light areas. Analyzed minerals are orthopyroxene, clinopyroxene, many of which are partially coated by ferric oxide and mantled by hornblende, and biotite, commonly jacketing ilmenite.

Most concentrates are better than 99 percent pure. Pyroxenes from rock 140 may contain as much as 2 percent hematite but close determination of its abundance is difficult because of a platy habit. Initially, there was some concern as to whether these extraneous Fe-oxide impurities in pyroxenes would significantly affect the Fe^{3+} determination, but the fact that the analyses of contaminated pyroxenes are in line with those of "pure" pyroxenes from 128 eliminates this possibility.

It was impossible to make a pure concentrate of the hornblende and the biotite from rock 154, owing to an overlap in densities and magnetic susceptibilities. The analyzed concentrate of hornblende contained, by

modal grain analysis, 6 percent of brown biotite. The biotite concentrate contained 6 percent hornblende; slight differences in pleochroism between biotite grains is obvious in an oil mount, about three-fourths are brown and the remainder greenish brown.

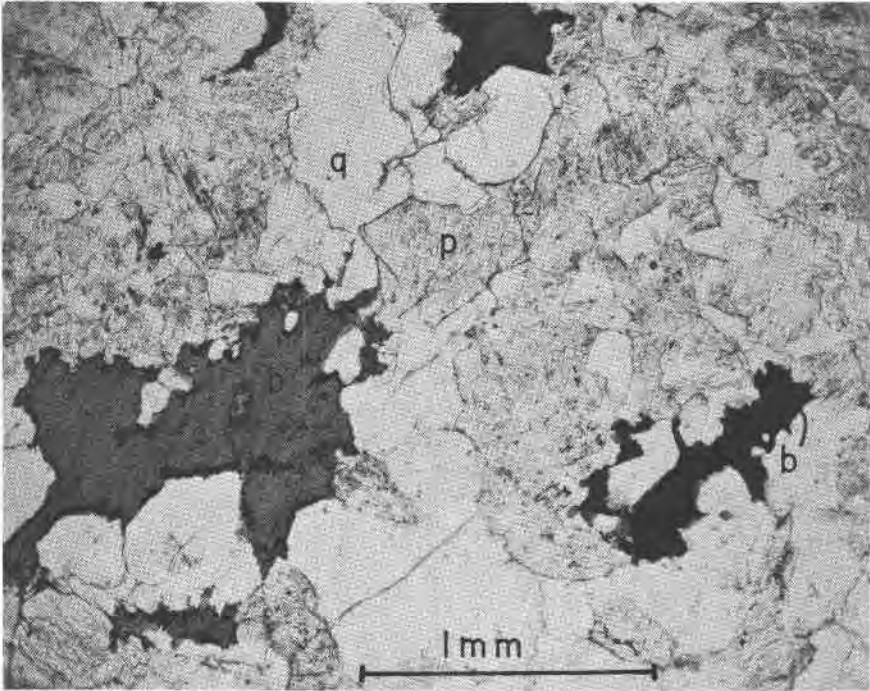


Fig. 6. Sample 148. Turbid perthite and clear quartz occur with ragged biotite grains.

PYROXENES

Chemistry of Pyroxenes. Chemical analyses of ten pyroxenes, nine of which are new, are set out in Table 2. In Table 3 the analyses are recast into numbers of cations on the basis of 6 oxygen, following method (2) of Bown (1964). The formula for pyroxenes which these numbers may be referred to is (Hess, 1949)



where W is Ca,* Na, K; X is Mg, Fe²⁺, Mn, Ni, Li; Y is Al, Fe³⁺, Cr, Ti; Z is Si, Al.

* To be consistent all ions should be identified by their valency, *e.g.*, Ca²⁺; however, for ease in typography only those ions with variable valence will be so identified. Where the valence of Fe is not indicated it is intended to mean the sum of Fe²⁺+Fe³⁺.

TABLE 2. CHEMICAL ANALYSES OF PYROXENES FROM THE GUADALUPE IGNEOUS COMPLEX

	140o	140c	128o	128c	132o	132c	153o	153c	83c ¹	106o ²
SiO ₂	53.64	52.32	52.77	52.51	51.81	52.03	49.27	51.20	n.d.	50.00
TiO ₂	0.42	0.59	0.33	0.37	0.40	0.34	0.43	0.27	n.d.	0.49
Al ₂ O ₃	1.47	1.97	1.12	2.11	1.26	2.15	0.94	0.80	n.d.	0.47
Fe ₂ O ₃	3.39	0.82	3.37	1.09	4.11	1.69	3.53	1.58	2.27	0.56
FeO	14.52	6.74	19.92	7.97	21.20	8.48	31.43	14.81	13.97	33.83
MnO	0.40	0.17	0.52	0.20	0.64	0.26	0.87	0.36	n.d.	0.84
MgO	24.72	15.75	21.06	14.23	19.39	13.69	12.43	10.27	10.57	11.51
CaO	1.62	21.26	1.15	21.58	1.28	21.23	1.38	20.37	18.86	1.74
Na ₂ O	0.03	0.31	0.04	0.28	0.06	0.33	0.04	0.32	n.d.	0.20
K ₂ O	0.02	0.04	0.02	0.04	0.04	0.02	0.04	0.06	n.d.	0.05
Total	100.23	99.97	100.30	100.38	100.19	100.22	100.36	100.04		99.69

¹ The original partial analysis of clinopyroxene 83 shown in Best (1963, Table 2) is erroneous because of orthopyroxene contaminant in the concentrate. A new concentrate was prepared and analyzed, for CaO and MgO, by E. L. P. Mercy.

² Analysis originally quoted in Best (1963, Table 2); includes 0.49 H₂O⁺ and 0.19 H₂O⁻.

TABLE 3. NUMBER OF IONS IN PYROXENES ON THE BASIS OF 6 OXYGEN ATOMS

	140o	140c	128o	128c	132o	132c	153o	153c	83c	160o
Si	1.945	1.935	1.960	1.945	1.946	1.938	1.946	1.967		1.998
Al	0.055	0.065	0.040	0.055	0.054	0.062	0.044	0.033		0.002
Al	0.008	0.020	0.009	0.037	0.002	0.032	0.000	0.003		0.020
Ti	0.012	0.016	0.009	0.010	0.011	0.010	0.013 ¹	0.008		0.017
Fe ²⁺	0.092	0.023	0.094	0.030	0.116	0.047	0.105	0.046		0.017
Fe ²⁺	0.440	0.208	0.619	0.247	0.666	0.264	1.038	0.476		1.129
Mn	0.012	0.005	0.016	0.006	0.020	0.008	0.029	0.012		0.029
Mg	1.336	0.868	1.165	0.785	1.086	0.760	0.732	0.588		0.686
Ca	0.063	0.842	0.046	0.856	0.052	0.847	0.058	0.839		0.074
Na	0.002	0.022	0.003	0.020	0.005	0.024	0.003	0.024		0.014
K	0.001	0.002	0.001	0.002	0.002	0.001	0.002	0.003		0.002
Z	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000		2.000
WXY	1.966	2.006	1.962	1.993	1.960	1.993	1.970	1.999		1.988
Mg	68.8	44.6	60.0	40.8	56.0	39.4	37.3	30.0	31.9	35.4
ΣFe	28.0	12.1	37.6	14.7	41.3	16.6	59.7	27.2	27.2	60.8
Ca	3.2	43.3	2.4	44.5	2.7	44.0	3.0	42.8	40.9	3.8
(ΣFe+Mn)100	29.1	21.4	38.5	26.5	42.5	29.6	61.6	47.6	46.2	63.5
ΣFe+Mn+Mg										

¹ 0.010 included in Z and 0.003 in Y.

The principal variation in the composition of clinopyroxenes is substitution of Fe^{2+} for Mg; the content of the other major cation, Ca, remaining very uniform throughout the sequence. Among minor constituents, Fe^{2+} is about twice as abundant in the Fe-rich clinopyroxene as in the Mg-rich. Ti appears to be more enriched in the high temperature (more magnesian) pyroxenes, as suggested by Verhoogen (1962a, p. 217).

Le Bas (1962) has characterized clinopyroxenes from various rock types with regard to SiO_2 vs Al_2O_3 in weight percent and to Al in Z vs TiO_2 weight percent. On these two bases the Guadalupe pyroxenes fall well within the fields for nonalkaline rocks (*i.e.* tholeiitic, high-alumina, and calc-alkaline). Further demonstration of the magma type from which these clinopyroxenes were derived is seen in their normative compositions. All contain hypersthene; 140, 128, and 132 have 4 to 1 percent olivine whereas 153 has a trace of quartz.

In the orthopyroxenes the principal variation is again in the substitution of Fe^{2+} for Mg. Comparison of the orthopyroxene analyses with those listed in, for example, Deer, *et al* (1962, vol. 2, Table 2), discloses nothing unusual, except that Fe^{3+} is uniformly higher in the Guadalupe orthopyroxenes. Normative calculations show 3 to 4 percent quartz in the analyses.

Although the partition of elements between coexisting crystalline phases will be considered briefly in a later section, it is worthwhile at this point to comment on the way in which the major cations Ca, Mg, and Fe^{2+} are distributed between the two pyroxenes, Figure 7 and 8, for this has a direct bearing on the crystallization of these particular pyroxenes from the Guadalupe magma. (Only meager information, mostly optical, is available on pyroxenes from petrographically similar calc-alkaline rock suites, but there is a suggestion that the partition in the Guadalupe and these suites are one and the same (Fig. 7). More data is desirable to prove this assumption.) The Guadalupe pyroxenes are compared with available data on igneous and metamorphic pairs in terms of Ca partition, Figure 8, and Fe^{2+} -Mg partition, Figure 9. On both grounds, the Guadalupe pyroxenes are more similar to pyroxenes from high-grade regional metamorphic rocks than to pyroxenes from tholeiitic magmas crystallized at low $f_{\text{H}_2\text{O}}$. The extreme values of Ca in the Guadalupe and metamorphic pyroxenes are especially noteworthy. That both Ca and Fe^{2+} -Mg partition values serve as characterizing parameters for different pyroxene suites has been pointed out by Bartholomé (1962). Thus when the atomic percent Ca, relative to $\text{Ca} + \text{Mg} + \text{Fe}$, in clinopyroxene > 45 , then the distribution constant, K_D , for Fe^{2+} -Mg in the coexisting pyroxenes is > 1.6 . When $\text{Ca} < 45$, $K_D < 1.6$.

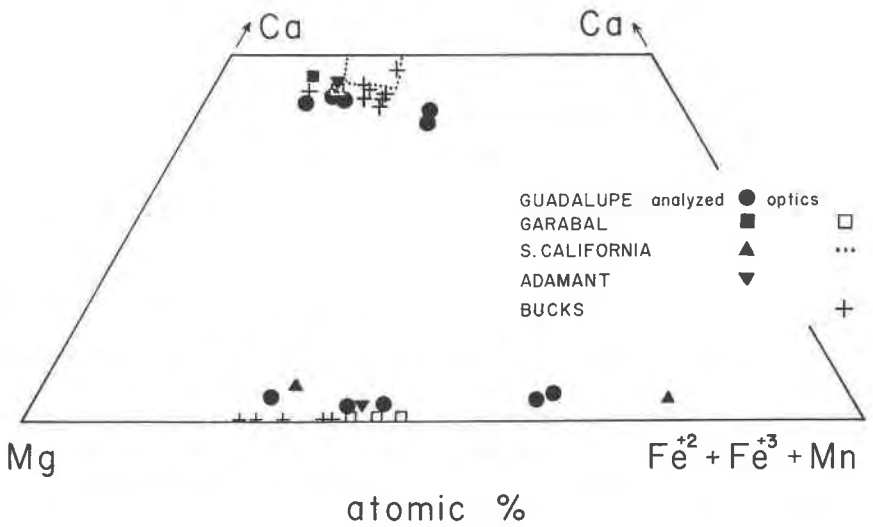


FIG. 7. Compositions of pyroxenes from the Guadalupe intrusion and other calc-alkaline plutonic suites. All the Ca-poor pyroxenes are orthorhombic and apparently most are not inverted pigeonite. The dotted enclosure at the top of the quadrilateral represents the variation in composition, based on optical measurements, of augites from the Southern California batholith (Larsen and Draisen, 1950). Data on pyroxenes in the Garabal Hill—Glen Fyne complex is from Nockolds and Mitchell (1948), on pyroxenes in the monzonitic Adamant Mountain (British Columbia) pluton from Fox (1965), and on pyroxenes in the zoned diorite-granite Bucks Lake pluton in the northern Sierra Nevada from Turner (unpublished).

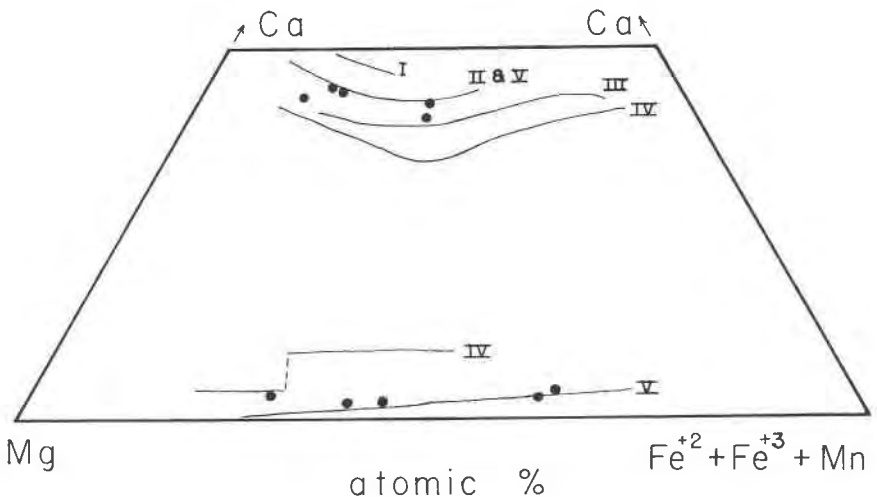


FIG. 8. Comparison of some trends of compositional variation in pyroxenes from different magmatic sequences and a metamorphic facies, with the calc-alkaline trend, exemplified by the Guadalupe pyroxenes (solid circles). The lines represent pyroxenes from the Black Jack sill, I, the Garbh Eilean sill, II, British and Icelandic Tertiary acid glasses, III, the Skaergaard intrusion, IV, (all from Deer *et al.*, 1963, vol. 2, Fig. 37) and from charnockites and associated granulites, V (Subramaniam, 1962).

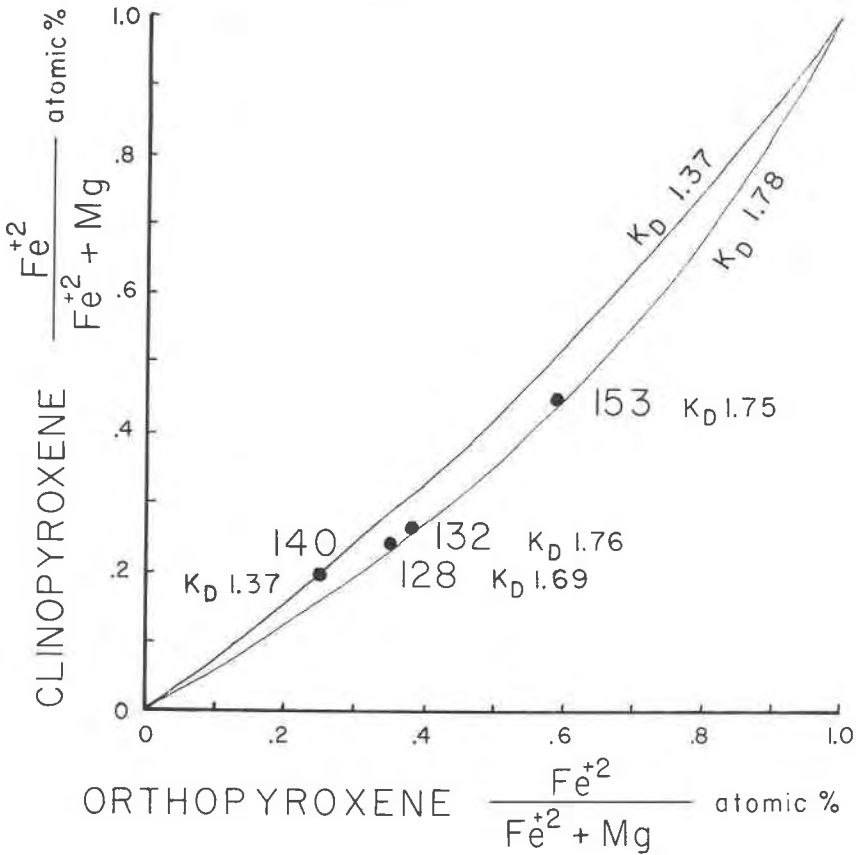


FIG. 9. Fe^{+2} -Mg distribution diagram for coexisting clinopyroxene-orthopyroxene pairs. Solid circles represent Guadalupe pyroxenes. Two distribution curves are drawn: $K_D=1.78$ is the best fit for pyroxene pairs from high-grade regional metamorphic rocks (Binns, 1962, Fig. 6); $K_D=1.37$ is the curve for igneous pyroxenes (data presented in logarithmic form in Bartholomé (1962, Fig. 6) and in inverted form in Kretz (1963, Fig. 1). $K_D = (Fe^{2+}/Mg)_{ortho}/(Fe^{2+}/Mg)_{clino}$.

Exsolution Effects in Pyroxenes. Salient textural features of exsolution lamellae in Guadalupe pyroxenes are summarized in Table 4 (see also Best, 1963, p. 233). It seems safe to assume that the (100) lamellae in orthopyroxene are augite, which is the conclusion of Hess (1960, p. 30), and Bown and Gay (1959, 1960). The nature of the lamellae in augites is less certain, however. Conventionally it has been thought (see for example Hess, 1960, p. 35) that clinopyroxenes more Fe-rich than about Fs_{15} exsolve (001) lamellae of pigeonite and then with further cooling of the pyroxene below the orthopyroxene-pigeonite inversion, these lamel-

TABLE 4. OPTICAL PROPERTIES AND NATURE OF EXOLUTION LAMELLAE IN PYROXENES

	140o	140c	128o	128c	132o	132c	153o	153c	83c	106o
Reflective indices and optic angle ¹										
α	1.682	1.684	1.694	1.684		1.691-1.696	1.719	1.696-1.698		1.715-1.725
β		1.689	1.704	1.689			1.732	1.700-1.720	1.700	1.735
γ	1.698	1.714	1.707	1.710	1.707-1.716		1.737	1.720-1.730		1.732-1.742
$2V_{\alpha}$	67		79	60	40-48		68			50-56
$2V_{\gamma}$		51				51		51	52	
Exsolution lamellae										
orientation	(100)	(100)	(100)	(001)	(100)	(001)	(100)	(001)	(001)	(100)
development	abundant, fine	abundant, planar	abundant	uncommon	abundant	common, fine	weak	abundant, uniform, very fine strings	abundant, uniform, very fine strings	(abundant, fine)

¹ All indices measured on analyzed concentrates in sodium light; determinations have a maximum error of $\pm .002$. Optic angles measured orthoscopically on a universal-stage by direct rotation between optic axes; maximum error less than $\pm 1^{\circ}$.

lae may invert to orthopyroxene with exsolution of (100) lamellae of Ca-rich pyroxene. Such second-order lamellae were described by Poldervaart and Hess (1951) and were presumed to have been found in a Guadalupe augite (Best, 1963, Fig. 4 and p. 235). However the anomaly in the Guadalupe pyroxenes is that, whereas in most instances the accompanying independently crystallizing Ca-poor pyroxene is pigeonite (which may subsequently invert to orthopyroxene), the coexisting pyroxene is orthopyroxene, with no evidence that it was at any time a pigeonitic pyroxene.

Other cases of anomalous exsolution in pyroxenes occur in the Mornington complex, New South Wales, from which Binns (1965, personal communication) reports pyroxenes similar to those in the Guadalupe, and in the Skaergaard intrusion, from which Bown and Gay (1960, p. 387) describe instances of pigeonite lamellae in augite coexisting with orthopyroxene, either primary or inverted from pigeonite. Bown and Gay (1960) suggest sluggish reaction rates prohibit inversion of pigeonite lamellae in augite, the similarity in structure of these two phases being a contributing factor.

Recently, Binns *et al* (1963) found that clinopyroxene lamellae in two augites examined by an electron microprobe are members of the clinostatite-clinoferrrosilite series. Some of the clinopyroxene in the lamellae is twinned, presumably on (100) (Binns, 1965, personal communication). Single crystal X-ray photographs of 106c disclosed the presence of monoclinic lamellae and the included second-order lamellae previously reported (Best, 1963) could actually be twinning, although the angular relations for the (100) law do not seem correct. Attempts with an electron microprobe to resolve Ca-contents of host and lamellae pyroxenes from the Guadalupe were unsuccessful because of their narrow width.

The discovery of Binns *et al* (1963) raises the important question as to how many presumed pigeonite lamellae are actually clinohypersthene. The existence of clinohypersthene as lamellae in augite would seem to simplify some aspects of exsolution phenomenon, particularly the compositional complexities of inversion of pigeonite lamellae to the less calcic orthopyroxene and the manner in which the Ca-content of these lamellae relate to the coexisting Ca-poor pyroxene phase. Unfortunately, the phase and polymorphic relations in Ca-poor magnesian pyroxenes are at present in a state of uncertainty, and considerably more definitive experimental work and complimentary analytic and crystallographic studies of natural pyroxenes are necessary before exsolution phenomenon will be understood.

The large difference between Ca-contents of the Guadalupe orthopyroxenes and clinopyroxenes might reflect granule exsolution of a subcalcic

augite at relatively low temperatures (approaching, perhaps, metamorphic temperatures) where the pyroxene solvus is close to the Di-Hd and En-Fs joins (J. M. Moore, personal communication, 1964). "Granule exsolution has been found in bornite-chalcopyrite solid solutions (Brett, 1962) and hypothesized in Fe-Ti oxide solutions (Vincent and Phillips, 1954; Buddington and Lindsley, 1964) and kalsilite-nepheline solutions (Sahama, 1960). It might then be expected to occur in pyroxene solid

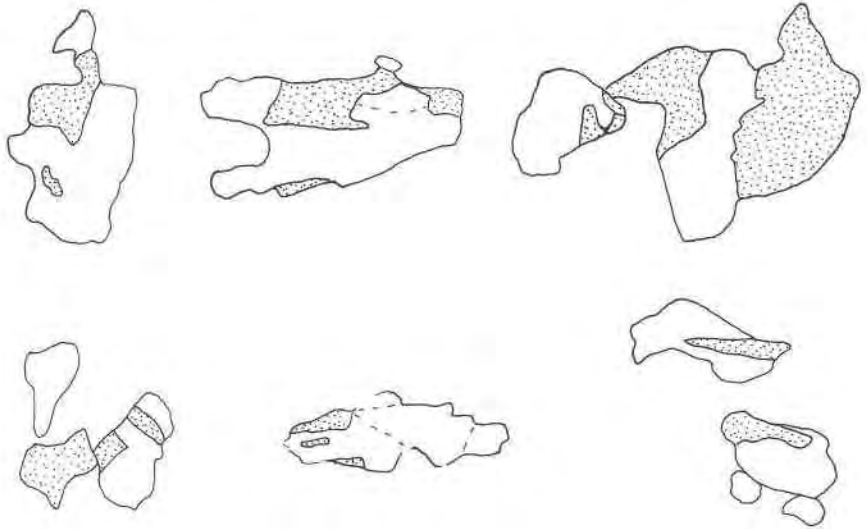


FIG. 10. Textural relations of some pyroxenes from Fe-rich gabbroic rocks (153 top and 83 bottom). Stippled pattern is clinopyroxene and plain is orthopyroxene, some parts of which have a mosaic texture (denoted by dashed lines) defined by slightly differing optical orientations. The larger grains are approximately one mm long.

solutions under favorable conditions, where the pyroxenes have cooled slowly for a prolonged period after crystallization. Pyroxenes in 140, 138 and 132 occur as independent grains, and this fact probably eliminates the possibility of granule exsolution. However in 153 and 83, aggregated, clino- and orthopyroxenes are present and examination of them with a universal-stage disclosed that several aggregates (see Fig. 10) have a special crystallographic orientation wherein Y orthopyroxene is 5° to 15° from X clinopyroxene. Poldervaart and Hess (1951) indicate these axes are coincident in lamellar exsolution. In some experimental work on unmixing of pigeonitic pyroxenes in basaltic melts at atmospheric pressure, I have observed identical crystallographic relations between the unmixed clino- and orthopyroxene phases as found in 153 and 83. The textures in the fine (about 0.3 mm) pyroxenes of 83 are especially reminiscent of the

synthetic pyroxenes. The observed composite grains in 153 and 83 possibly crystallized as a phase close to pigeonite in composition, judging from the larger proportion of orthopyroxene relative to clinopyroxene. The aggregated grains are slightly randomized, but as McDougall (1961, p. 682) notes, ". . . A single pigeonite crystal, on inversion, has given rise to two or more areas of orthopyroxene which have different orientations."

In 83 virtually all orthopyroxene occurs intimately with clinopyroxene, and in the absence of independent and undoubted primary grains it appears probable that orthopyroxene resulted only through unmixing of primary pigeonitic pyroxene. Many grains of clinopyroxene occur without attached orthopyroxene and thus are considered primary. In 153 there appear to be primary independent orthopyroxenes and clinopyroxenes, as well as the aggregated clusters.

Crystallization of the Pyroxenes. Considerable attention has been given to the trends of crystallization of plutonic pyroxenes, and for recent summaries and reviews of the literature one can refer to Deer *et al* (1962, vol. 2, p. 125), Brown and Vincent (1963), or Boyd and Schairer (1964). Special note should be made of the course of crystallization of the Guadalupe pyroxenes, however, because of the following: (1) the Guadalupe Ca-poor pyroxenes are orthopyroxenes throughout the entire sequence of gabbroic rocks. Although pigeonite has always been reported as the pyroxene more Fe-rich than about Fs_{30} in differentiated bodies, there is no firm evidence for its former presence in the Guadalupe, except possibly for the most Fe-rich gabbros (*e.g.* 83 and 153) where Ca-poor pyroxene is Fs_{60} . (2) Ca-rich clinopyroxenes show only a small variation in CaO, about 1.2 weight percent (excluding the anomalously textured (83)). (3) The partition of Ca, Mg, and Fe^{2+} between the coexisting clinopyroxene and orthopyroxenes appears, on the basis of meager data, to be similar to that in other calc-alkaline plutonic suites. Essentially the same partition is found in high-grade regional metamorphic rocks. The Ca-rich Guadalupe pyroxenes show a trend comparable to those in differentiated alkali gabbros lacking an associated Ca-poor pyroxene. (4) Abundant hydrous minerals occur in even the early gabbroic differentiates of the Guadalupe.

These facts suggest the course of pyroxene crystallization in the Guadalupe gabbros was conditioned by relatively high water fugacities and low temperatures close to those prevailing during high-grade regional metamorphism. If the suspected autometamorphism in the middle gabbros actually occurred, then those constituent pyroxenes were conditioned in their distribution of Mg, Fe, and Ca by metamorphic conditions. However, the more Fe-rich and Fe-poor gabbroic rocks have more

typical igneous textures but their constituent pyroxenes also show essentially the same distributions of major ions.

Deer and Abbott (1965) have described Ca-rich clinopyroxenes from a differentiated gabbroic intrusion in east Greenland. The Ca-contents are high, similar to the Guadalupe, and this property, together with a limited Fe-enrichment, is attributed to higher water-vapor pressures, inasmuch as intercumulate chlorite, amphibole, and epidote are common in the gabbros. Interestingly, practically no Ca-poor pyroxene occurs in these rocks.

The limited Fe-enrichment in Ca-rich clinopyroxenes from hydrous differentiated mafic intrusions is related mainly to the fact that such magmas leave the field of stable pyroxene when only moderately enriched in Fe, hornblende and biotite then taking over completely as ferromagnesian silicates. No marked change in partition of Fe between liquid and pyroxene likely occurs, except for that occasioned by the induced depression of crystallization temperatures. The Ca-rich clinopyroxenes in the Garabal Hill—Glen Fyne complex, a Caledonian calc-alkaline plutonic suite (Nockolds and Mitchell, 1948), show, on the basis of optical properties, that this hydrous magma also ceased to crystallize pyroxenes at about the same Fe/Mg ratio as did the Guadalupe.

The details of crystallization of the Guadalupe pyroxenes can best be understood by referring to the hypothetical equilibrium diagrams for pyroxenes presented by Muir (1954; also reproduced in Deer *et al.*, 1962, vol. 2, Fig. 38) and to Figure 11. Figure 11(a) and (b) are TX sections through the T-Di-En-Fs-Hd prism containing the analyzed Guadalupe pyroxene pairs 128 to 153, respectively. Schematic partial isothermal sections corresponding to (a) and (b) are shown as (c) and (d), respectively (compare with Roedder (1965) and Yoder *et al.* (1964)).

Figure 11(a) and (c), utilizing the pair 128, are assumed to be representative of the general phase relations during crystallization of the Mg-rich and middle gabbros,¹ or 140, 128, and 132; (b) and (d) represent pyroxene relations in the Fe-rich gabbros, or 83 and 153. In Figure 11(a), the dashed lines depict the usual phase relations in a basaltic magma which is crystallizing "dry" or under low f_{H_2O} (after Muir, 1954). The primary pyroxenes precipitating from the magma are augite and pigeonite; at a somewhat lower temperature on the flat top of the solvus, the pigeonite unmixes to orthopyroxene with minor augite (as lamellae). In a magma crystallizing under relatively high f_{H_2O} the pyroxene liquidus would be depressed, to the extent shown schematically by solid lines. In

¹ Possible autometamorphism of middle gabbros is not considered here.

this case the pyroxenes in equilibrium with the eutectic liquid would be orthopyroxene and augite whose Ca-contents are more extreme than for the low f_{H_2O} pyroxene pairs. The region of the solvus likely to be involved at high f_{H_2O} has steep slopes. Boyd and Schairer (1964, Figure 1) show in

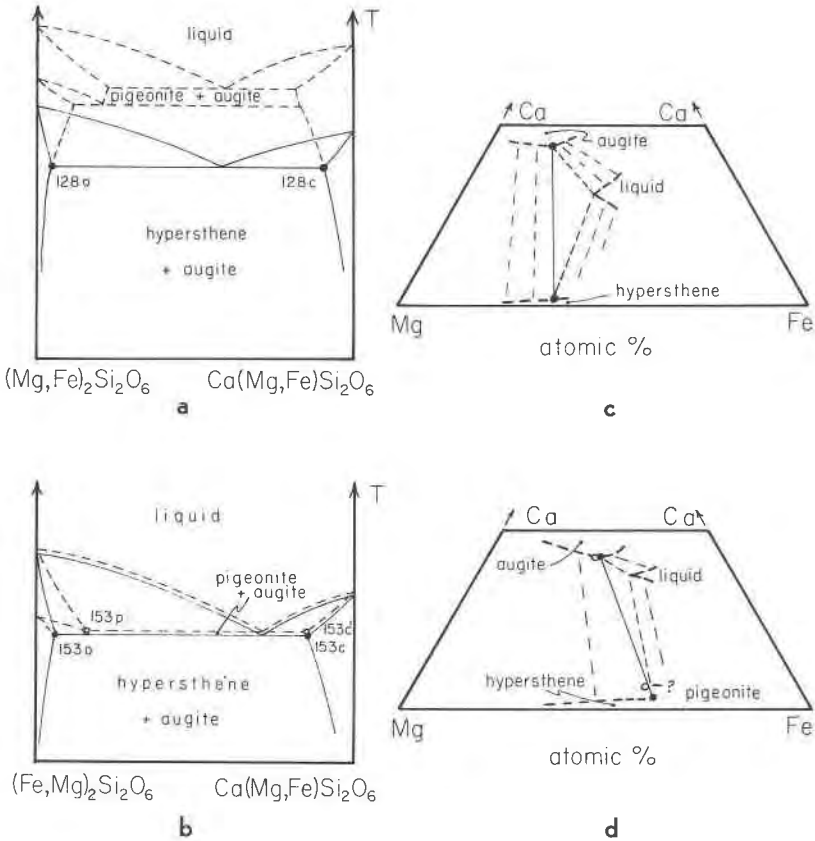


FIG. 11. Hypothetical phase diagrams to aid in the understanding of crystallization of the Guadalupe pyroxenes. See text for discussion.

the system En-Di the solvus boundary shifts by only a few weight percent $CaSiO_3$ between $900^\circ C$ to $700^\circ C$.

In 83 there is textural evidence that the primary pyroxenes were Ca-rich clinopyroxene and a pigeonitic pyroxene, which unmixed to the observed composite grains of orthopyroxene with minor clinopyroxene. Equilibrium relations during crystallization of pyroxenes in 83 may have approximated those proposed by Muir (1954) for dry systems. The rock

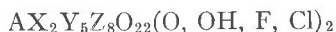
153 is much coarser, has a greater percentage of hydrous minerals, and also occurs nearer the postulated top of the Guadalupe complex. It carries what appear to be primary independent grains of Ca-rich clinopyroxene and orthopyroxene, as well as aggregated grains of these phases which may represent granular exsolution of a primary pigeonitic phase. If these textural relations are interpreted correctly then the formation of the 153 pyroxenes may have been governed by the phase relations shown in Figure 11(b). Initially a pigeonitic pyroxene 153p together with a Ca-rich clinopyroxene 153c' precipitated from the liquidus (note dashed phase boundaries in Fig. 11(b)). If the field of pigeonite plus augite had been reduced to a very thin band at the Fe:Mg ratio of 153, then a small increase of f_{H_2O} subsequent to crystallization of the early 153p and 153c' would have eliminated this band altogether such that liquid would be in equilibrium with pyroxenes 153o and 153c. Simultaneously with the precipitation of these two pyroxenes, the early 153p grains might unmix to 153o and 153c, provided the temperature had dropped slightly as f_{H_2O} increased. Note that the compositions of 153c' and 153c would be very nearly the same.

If precipitation of hydrous Fe-Mg silicates had not taken the place of pyroxenes in the residual magma remaining after formation of rock 153,¹ an Fe-rich pigeonitic trend may have been more firmly established. It appears that at the composition of 153 the two-phase region of pigeonite plus augite in the pyroxene—temperature quadrilateral prism was barely intersected. The phase relations of more Fe-rich pyroxenes, had they precipitated, would have been dependent on a thickening wedge of this region. The pyroxenes in 83 probably were involved in this thicker two-phase region, not because of a greater degree of Fe-enrichment but apparently because of locally lower f_{H_2O} .

The delicate exsolution lamellae seen in the Fe-rich pyroxenes took place after any granule exsolution which might have occurred.

HORNBLENDES

The analyses of the hornblendes have been recalculated in Table 5 on the basis of 24 anions into a general formula



where

X = Ca, Na, K; Y = Mg, Li, Ti, Fe²⁺, Fe³⁺, Mn, Al; Z = Si, Al.

¹ It is interesting to note that Nockolds and Mitchell (1948) found similarly Fe-enriched pyroxenes (by optical properties) in Caledonian rocks and beyond which in later, more silicic differentiates hydrous ferromagnesian silicates took the place of pyroxenes. Presumably in such magmas crystallizing at high f_{H_2O} the liquid of this composition leaves the field of stable pyroxene.

TABLE 5. HORNBLENDSES

Chemical Analyses				
	128h	132h	153h	154h ¹
SiO ₂	46.12	43.64	44.48	41.97
TiO ₂	2.38	2.67	1.69	1.45
Al ₂ O ₃	9.27	9.80	7.47	8.39
Fe ₂ O ₃	2.09	2.85	3.91	6.16
FeO	10.42	12.22	17.70	21.77
MnO	0.11	0.15	0.26	0.48
MgO	13.95	12.28	9.34	3.73
CaO	11.62	11.75	10.72	10.85
Li ₂ O	0.01	0.04	0.04	0.04
Na ₂ O	1.55	1.73	1.46	1.68
K ₂ O	0.54	0.69	0.97	1.22
H ₂ O ⁺	1.60	1.94	1.47	2.14
F	0.10	0.09	0.31	0.41
Total	99.76	99.85	99.82	100.29
Less O for F	0.04	0.04	0.13	0.16
Total	99.72	99.81	99.69	100.13
Number of ions on the basis of 24 (O, OH, F)				
Si	6.475	6.463	6.782	6.511
Al	1.255	1.537	1.213	1.489
Al	0.343	0.173	0.125	0.041
Ti	0.264	0.294	0.193	0.168
Fe ³⁺	0.228	0.320	0.440	0.728
Fe ²⁺	1.273	1.513	2.253	2.826
Mn	0.018	0.018	0.037	0.065
Mg	3.039	2.715	2.126	0.867
Li	0.004	0.016	0.018	0.018
Ca	1.818	1.869	1.750	1.800
Na	0.440	0.498	0.440	0.504
K	0.106	0.124	0.184	0.242
OH	1.564	1.922	1.502	2.220
F	0.044	0.045	0.147	0.205
(ΣFe+Mn)100	33.3	40.8	56.2	80.4
ΣFe+Mn+Mg				
Optical properties ²				
α	1.657 pale brown	1.661 pale brown	1.671 pale brown	1.662 pale brown
β	1.672 brown	1.676 brown	1.684 green-brown	1.683 deep olive-green
γ	1.680 dark brown	1.686 dark smokey brown	1.697 olive-green	1.689 dark bluish green
2V _α	74	55	56	
γ∧c	13	17	16	

¹ Corrected for 6 percent biotite 154b.² See footnote Table 5.

The position A is not occupied in the ideal tremolite end member $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH}, \text{F})_2$ but in aluminous hornblendes there is generally an excess of K and Na over that required, along with Ca, to bring X to 2.00, and this excess, together in certain instances with H, goes into the A position (Phillips, 1963).

All of the Guadalupe hornblendes, though ranging widely in the degree of substitution Fe^{2+} -Mg, are common hornblendes or aluminous calciferous amphiboles, according to the nomenclature of Deer *et al* (1962, vol. 2, p. 271), and Phillips and Layton (1964).

The number of Si, Al, Ca, and Na ions fluctuate with respect to the Si content of the host rock. However, with respect to increasing Si in the rock, Ti and Mg decrease, whereas Fe^{3+} , Fe^{2+} , Mn, Li, K and F increase.

The Guadalupe hornblendes compare rather closely to those from similar rock types in other intrusions. Ti is higher, however, than in hornblendes from the Southern California batholith reported by Larsen and Draisin (1950). Normative calculations indicate all the Guadalupe hornblendes contain olivine; 154a and 132a carry in addition nepheline.

BIOTITES

The three biotites analyzed from the Guadalupe complex are not unlike Fe-dominant "trioctahedral" micas occurring in other calc-alkaline intrusive rocks (see Foster, 1960; Deer *et al.*, 1962, vol. 3, pp. 76-78). Calculation of the number of ions, shown in Table 6, suggests that certain variations occur as a function of host rock. Thus from quartz-bearing, Fe-rich gabbro through quartz monzonite to granite (rocks containing, respectively, two pyroxenes and hornblende, hornblende alone and no other mafic silicate) there are increases in Al (particularly evident as an increase in octahedrally coordinated Al), Fe^{3+} , Na and (OH) and a decrease in K and the overall number of 6- and 12-coordinated cations. The ratio $\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}:\text{Mg}$, which generally increases in minerals from differentiated igneous sequences, is erratic.

Although the number of octahedral sites occupied in 148b is only 5.1, compared to the theoretical 6.0 in an ideal trioctahedral mica, there are compensating charge contributions from the abundant Al, Ti, and Fe^{3+} . The composite layer charge in this mica balances reasonably well with the interlayer cationic charge, following the convention of Foster (1960) in calculating structural formulae.

The three biotites are plotted in Figure 12 which portrays the relations between octahedrally coordinated Mg, Fe^{2+} , and $\text{Al} + \text{Fe}^{3+} + \text{Ti}$. For comparison, the fields of phlogopite, Mg- and Fe-biotite, and siderophyllite-lepidomelane defined by Foster (1960, Fig. 11) are shown. The field of biotite comprises micas from granites, quartz monzonites, diorites,

TABLE 6. BIOTITES

Chemical Analyses			
	153b	154b ¹	148b
SiO ₂	35.93	35.63	37.71
TiO ₂	4.27	3.17	2.68
Al ₂ O ₃	13.00	13.17	14.31
Fe ₂ O ₃	2.61	6.67	10.21
FeO	20.81	24.83	15.28
MnO	0.11	0.33	0.20
MgO	9.26	2.67	5.98
CaO	0.41	1.67	0.88
Li ₂ O	0.15	0.14	0.14
Na ₂ O	0.10	0.33	0.40
K ₂ O	10.14	7.83	7.78
H ₂ O ⁺	2.69	2.83	4.21
F	0.65	1.17	0.14
Total	100.13	100.44	99.92
Less O for F	.27	.50	.06
Total	99.86	99.94	99.86

Number of ions on the basis of 24 (O, OH, F)

Si	5.604	5.608	5.686
Al	2.396	2.392	2.314
Al	0.004	0.048	0.260
Ti	0.497	0.378	0.308
Fe ³⁺	0.300	0.794	1.158
Fe ²⁺	2.718	3.272	1.928
Mn	0.019	0.047	0.027
Mg	2.155	0.624	1.340
Li	0.094	0.094	0.090
Ca	0.066	0.284	0.145
Na	0.038	0.094	0.108
K	2.024	1.570	1.502
F	0.319	0.586	0.063
OH	2.792	2.970	4.236
(ΣFe+Mn)100	58.5	86.8	70.0
ΣFe+Mn+Mg			

Optical properties²

(β+γ)/2	1.664-1.670	1.637	1.665-1.674
γ	light brown	light yellow-brown	light yellow-brown
β	dark red-brown	brown-black	brown-black
γ	dark red-brown	brown-black	brown-black

¹ Corrected for 6 percent hornblende 154h.² See footnote Table 5.

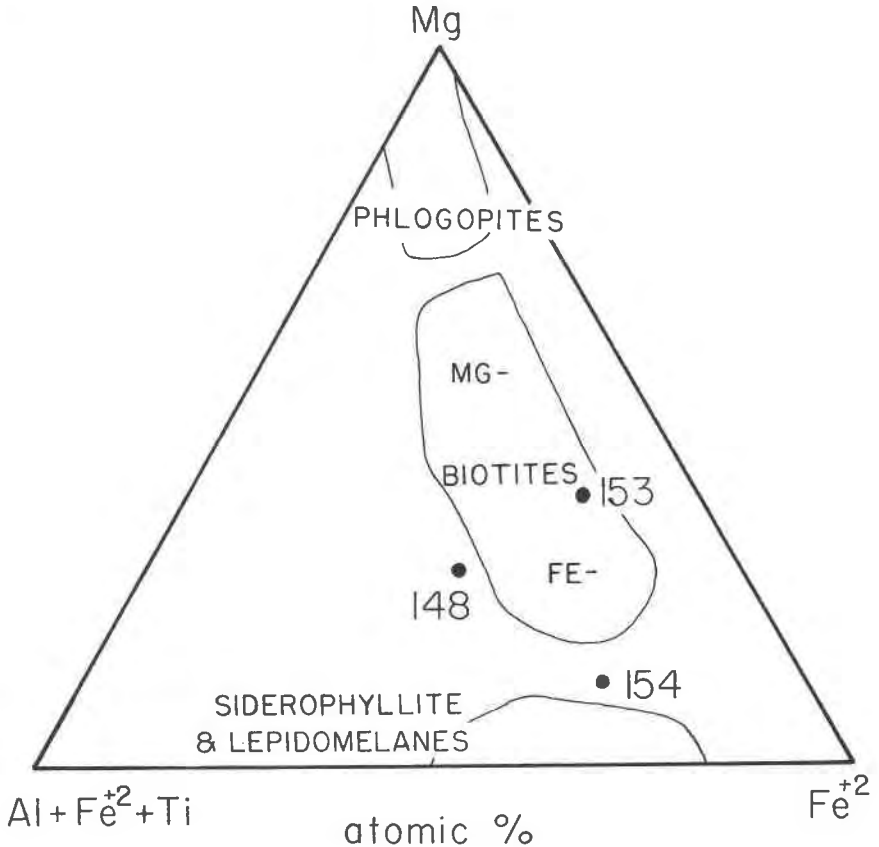


FIG. 12. Octahedrally coordinated cations in trioctahedral micas. Solid circles are Guadalupe biotites. Fields of natural biotites are taken from Foster (1960, Fig. 11).

syenites, and nepheline syenites with no visible clear-cut distinction between rock types (Foster, 1960, Fig. 12). Similar triangular diagrams, presented by Heinrich (1946), which employ oxide percentages seem to show a better correlation between biotite and host rock type. Thus, the aforementioned ionic variations (note again the $Fe^{2+}+Fe^{3+}+Mn:Mg$ ratios) in the Guadalupe biotites should be viewed with caution, there being the possibility that more analyses would modify any trends based on the limited data presented.

ILMENITES

Chemical analyses of ilmenites together with the calculated cationic abundances referred to 6 oxygen are shown in Table 7. The ideal formula

for ilmenite, FeTiO_3 , is never satisfied in natural material, there always being additional divalent cations Ca, Mg, Mn, etc., substituting in the place of Fe^{2+} . Moreover, there is limited solubility (up to 6 wt. percent; see Deer *et al*, 1962, vol. 5, p. 30) of the hematite "molecule" Fe_2O_3 in the rhombohedral structure of ilmenite. Small amounts of Al^{3+} and V^{3+} pos-

TABLE 7. ILMENITES

Chemical Analyses			
	128i	132i	153i
SiO_2	0.49	0.62	0.60
TiO_2	51.78	50.56	51.49
Al_2O_3	0.21	0.26	0.18
V_2O_5	0.10	0.10	0.04
Fe_2O_3	6.49	8.03	6.04
FeO	37.81	38.14	40.27
MnO	0.57	0.69	0.84
MgO	2.34	1.56	0.52
CaO	0.09	0.15	0.07
Total	99.88	100.11	100.05
Number of ions on the basis of 6 O			
Si	0.024	0.030	0.029
Al	0.012	0.015	0.010
V	0.004	0.004	0.002
Fe^{3+}	0.239	0.297	0.221
Ti	1.909	1.872	1.882
Fe^{2+}	1.550	1.570	1.637
Mn	0.024	0.029	0.034
Mg	0.171	0.114	0.038
Ca	0.005	0.008	0.003

sibly occupy permissible Fe^{3+} sites. With regard to Si^{4+} , Vincent and Phillips (1954, p. 19) suggest ilmenites can accommodate as much as 0.5 weight percent. Part of the SiO_2 indicated in the Guadalupe analyses is due to adhering pyroxene and biotite contaminant, but part may belong to the oxide phase.

There are several alternative explanations for the deviation of molecular proportions of tetra- and divalent cations from the ideal formula in the Guadalupe ilmenites, as follows (see for example, Buddington and Lindsley, 1964, p. 328): (1) The molecular excess of Ti over $\text{Fe}^{2+} + \text{Mg}$

+Mn+Ca is due to an excess of TiO_2 at the time of formation of the ilmenites. The excess permitted in solid solution is, however, very limited at 1300°C (Taylor, 1964) and at significantly lower temperatures is probably less. Therefore the apparent excess of TiO_2 in the Guadalupe ilmenites (shown by the plotted points in Fig. 13) is considered too great for a solid solution phenomenon. Moreover, the ilmenites are homogeneous optically and with respect to X-ray diffraction, ruling out the possibility that they might be two-phase entities, such as ilmenite plus

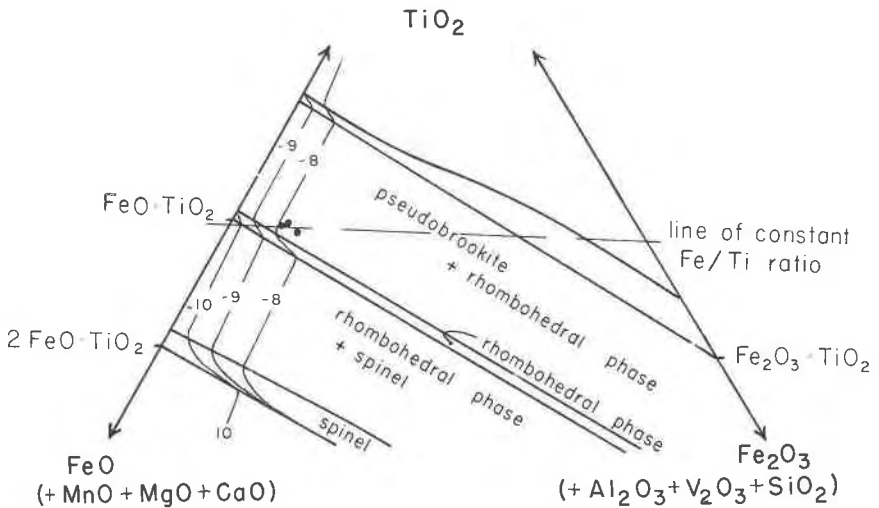


FIG. 13. Phase relations in a part of the system $\text{FeO-TiO}_2\text{-Fe}_2\text{O}_2$ at 1300°C (after Taylor, 1964). Oxygen isobars (values are of $\log f_{\text{O}_2}$) are linear in two-phase regions and curved in one-phase. Guadalupe ilmenites, shown as solid circles, are plotted in terms of all the oxides indicated.

rutile. (2) Unreported divalent cations could compensate for an apparent excess of Ti. All the analyses, however, total very close to 100 percent, leaving no chance for this possibility. (3) Some Fe^{2+} originally present has been oxidized, probably during slow cooling of the ilmenite from magmatic temperatures. Oxidation during weathering or during laboratory processing of the concentrate for chemical analyses doesn't seem likely in view of the fresh appearance of the ilmenites in polished section, and of the concentrates under a binocular microscope. Because explanations (1) and (2) are without support, and because there is no evidence against (3), it is taken to be the most rational explanation. (The same conclusion for other ilmenites is drawn by Taylor, 1964, p. 1028.) Utilizing the line of constant Fe/Ti ratio in Figure 13, the Guadalupe

ilmenites can be reduced towards the join $\text{FeO}-\text{TiO}_2$ yielding a composition of approximately $\text{hem}_3\text{ilm}_{97}$ which was very probably the stable homogeneous phase initially crystallizing from the Guadalupe magma.

The compositions of the analyzed ilmenites reflect the position of their host rocks in the differentiation sequence. With respect to rising silica content of the rock, Mg^{2+} decreases fourfold, Fe^+ increase about 10%, and Mn^{2+} increases 40%.

PARTITION OF ELEMENTS BETWEEN COEXISTING CRYSTALLINE PHASES

Although it is a fairly routine procedure to separate and analyze constituent minerals from igneous rocks, the interpretation of the manner in which ions from the magma have been distributed between the several crystallizing phases is open to considerable uncertainty. The most serious difficulty is the fact that most igneous rocks are produced by precipitation of crystals from a magma over a *range* of temperature, and/or pressure. The extent to which equilibrium between the compositions of crystal and liquid is achieved is subject to numerous factors, one of the most significant being the rate of cooling of the magma. Zoned crystals in an igneous rock are generally interpreted as evidence for incomplete reaction, or a failure to maintain equilibrium, between crystals and liquid. Certain textures may be interpreted as evidence that a particular phase crystallized prior to another (or others). Yet one must keep in mind the possibility that although, for example, hornblende is interstitial to euhedral pyroxene and feldspar, the three phases could well be an equilibrium assemblage because slow cooling, perhaps aided by abundance of volatiles as catalyzers, permitted continuous and complete reaction between the three crystalline phases and liquid as the temperature changed.

Apart from these uncertainties, the processing of the rock by human hands imposes some bias in what is concentrated from the rock and the way in which it is chemically analyzed.

In the Guadalupe samples, compositional zoning in plagioclase is ubiquitous, and some variability in optical properties, density, and magnetic susceptibility was noted in the ferromagnesian silicates analyzed. In most rocks yielding minerals for analyses, no evidence of marked textural disequilibrium was found (see Figs. 2 to 6). The exception is sample 153, in which it appears that much of the pyroxene crystallized prior to hornblende and that biotite generally followed ilmenite. In the absence of independent data, such as might be provided by an electron microprobe, it is impossible to state just how homogeneous the analyzed minerals are, or the extent to which coexistence in the rock is indicative of compositional equilibrium at the time of crystallization. Graphical analyses of the Guadalupe pyroxene compositions utilizing plots applied

to other pyroxene associations suggest an approach to equilibrium with respect to these two phases.

With these important assumptions and reservations in mind, some of the salient aspects of ion partition in the coexisting Guadalupe minerals may now be examined. With regard to hornblende and biotite, the partition is comparable in most respects to that in another calc-alkaline plutonic suit—the rocks of the Southern California batholith (Larsen and Draisin, 1950) and to that in schists described by Nickel (1954). In more general terms, the partition of ions between the two coexisting pyroxenes, hornblende, and biotite is generally similar to that demonstrated in miscellaneous data collected by Devore (1957). Scrutiny of the partitions discloses, however, certain anomalies. Devore (1957), for example, emphasizes that in coexisting clino- and orthopyroxenes the former are enriched in Fe^{3+} and Ti. In the Guadalupe, Fe^{3+} is more abundant in orthopyroxene and Ti is not consistently enriched in the clinopyroxene.

The chemical analyses essentially confirm what was shown in Best (1963, Fig. 6) on optical grounds, *viz.*, that for similar plagioclase composition the Guadalupe pyroxenes are not nearly as enriched in Fe as are those in the Skaergaard. This follows, presumably, from the relative Fe-enrichment in these two magmas.

INFLUENCE OF $f_{\text{H}_2\text{O}}$ AND f_{O_2} ON THE COMPOSITIONS OF MINERALS

The reconnaissance hydrothermal experiments of Yoder and Tilley (1962, especially Figs. 27 and 28) indicate that for a particular temperature interval, as $f_{\text{H}_2\text{O}}$ (they plot $p_{\text{H}_2\text{O}}$) increases in a basaltic magma, amphibole becomes a more dominant ferromagnesian phase, taking the place of pyroxene and olivine. The modal data on Guadalupe gabbroic rocks (see Best, 1963) provide a natural example of this phenomenon. Olivines disappear early in the differentiation sequence, at about the same position as hornblende becomes a prominent constituent; the last pyroxenes appear in the Fe-rich gabbroic rocks, which contain abundant hornblende and biotite. In all the more silicic differentiates hornblende and biotite are the sole ferromagnesian silicates.

To this rather direct implication of relatively high $f_{\text{H}_2\text{O}}$ in the Guadalupe magma should be added the effect it had on the distribution of Ca, Mg, and Fe^{2+} in the pyroxenes.

The f_{O_2} in a crystallizing magma can be evaluated, to a certain degree, by examination of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in the Fe-bearing phases, and indirectly by assessing the nature of coexisting Fe-bearing silicates, oxides, and sulfides. Pertinent data along these lines for the Guadalupe include:

- (1) Pyroxenes, particularly Ca-rich clinopyroxenes, are not abnormally enriched in the $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ molecule, as they would be if crystal-

lized at high f_{O_2} . (In unpublished experiments by the writer, yellowish Fe^{3+} -rich clinopyroxenes ($2V \sim 60^\circ$, and $\gamma \wedge C = 50^\circ$) have been synthesized when the 1887 Mauna Loa (Hawaii) basalt was held at approximately $1150^\circ C$ in the presence of a nickel-nickel oxide buffer ($f_{O_2} \sim 10^{-8.5}$) at one atmosphere total pressure. In contrast, with a wüstite-iron buffer ($f_{O_2} \sim 10^{-12.5}$) the clinopyroxenes have the normal amount of Fe^{3+} found in typical tholeiites.) In fact, the number of Fe^{3+} ions in the Guadalupe clinopyroxenes is no greater on the average than those from the Skaergaard (Brown, 1957) intrusion, commonly regarded as crystallizing under low f_{O_2} .

(2) Sulfides appear only sparingly and are confined to the Mg-rich gabbros.

(3) Ilmenite is, with minor exceptions, the dominant Fe-Ti oxide in gabbroic rocks; magnetite, with (111) lamellae of ilmenite, occurs locally. Similar magnetite plus independent ilmenite grains constitutes the oxide assemblage in quartz-rich differentiates.

(4) The rather high ratios of Fe_2O_3/FeO previously reported for bulk rocks (Best, 1963, p. 256) appear too high, in view of the low ratios found in all the analyzed Fe-bearing mafic silicates constituting these rocks. Barring the remote possibility of excessive amounts of Fe^{2+} in plagioclase (they are actually colorless or rarely white) the high ratios must be related to the ubiquitous films of secondary ferric oxide which pervade grain boundaries and internal fractures and cleavages. A rough calculation of the Fe_2O_3/FeO weight percent ratio for 153, based on its mode and mineral compositions yields 0.15, compared to 0.24 for the bulk rock analysis (Best, 1963, Table 5).

The discussion which follows is an attempt to obtain approximate values for f_{O_2} during crystallization of the Guadalupe magma.

Compositions of the Guadalupe ilmenites have been plotted in Figure 13, taking into consideration all the analyzed oxides, together with the one and two phase fields and isobaric tie lines in the simple system $FeO - Fe_2O_3 - TiO_2$ at $1300^\circ C$ and one atmosphere total pressure (Taylor, 1964). Assuming that the phase fields in the natural system at the temperatures of crystallization of the Guadalupe gabbroic rocks (presumed to be about $1100^\circ C$ to $900^\circ C$) are essentially the same as those for the ternary system at $1300^\circ C$,¹ then certain inferences can be made regarding the f_{O_2} at which ilmenite crystallized and cooled. The plotted points rep-

¹ Lindsley (1965) reports that pseudobrookite solid solutions ($FeTi_2O_5 - Fe_2TiO_5$) decompose from $1140^\circ C$ to about $600^\circ C$ to ilmenite-hematite solid solutions plus rutile. These findings do not modify the arguments and conclusions presented herein, provided the excessive TiO_2 contents of the Guadalupe ilmenites are apparent only, being produced by slight post-crystallization oxidation.

represent the homogeneous pure Guadalupe ilmenites, but because they fall in the two-phase field, pseudobrookite and rhombohedral phase, they must have become oxidized somewhat, subsequent to crystallization in the one-phase band. The initial composition is approximated by extrapolating into the one-phase band along a line of constant Fe/Ti ratio, giving an original composition of about $\text{hem}_3\text{ilm}_{97}$. At 1300°C this composition is in equilibrium with an f_{O_2} of 10^{-9} bars. The f_{O_2} at lower temperatures can be read from the $\text{hem}_3\text{ilm}_{97}$ contour line in Buddington and Lindsley (1964, Fig. 5), giving at 1100°C approximately $10^{-10.5}$ and at 900°C $10^{-13.5}$. During cooling of the ilmenite to lower temperatures, the f_{O_2} must have increased one or two orders of magnitude relative to the $\text{hem}_3\text{ilm}_{97}$ contour line to account for the observed oxidation. Buddington and Lindsley (1964) discuss a hypothetical magma at 1000°C , fluid pressure (mainly H_2O) of 1000 bars, and f_{O_2} $10^{-10.4}$ bars which, upon cooling as an open system to 500°C at the same fluid pressure has f_{O_2} 10^{-24} bars. A comparable decrease in f_{O_2} in the Guadalupe wouldn't have caused any oxidation of the ilmenites (refer to their Fig. 5). (There would have been, however, major oxidation of a spinel phase under these conditions, had such been present.) To account, then, for the slight oxidation in the ilmenites one can only postulate preferential loss of H_2 , or possibly sulfur compounds, from the intergranular fluids in the gabbros during cooling.

Apart from the information of f_{O_2} in the Guadalupe magma provided by experimental data on ilmenite stability, the f_{O_2} may also be approximated by consideration of equilibria among the volatile constituents¹ of a plutonic magma. Numerous factors affect the equilibrium relations, and simplifying assumptions must be made when calculating fugacities of different volatiles. The equilibria will be affected by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the melt, but as pointed out by Verhoogen (1962b, p. 174), the volatile constituents and their proportions will be the controlling factors because of their very large molecular proportions relative to Fe in the melt.

Consider a magma system at 1400°K (1127°C), $f_{\text{H}_2\text{O}} = 500$ bars, and $p_{\text{total}} \sim 5000$ bars, *i.e.*, the conditions under which the Guadalupe magma is presumed to have begun to crystallize. What is the equilibrium f_{O_2} ? Under the conditions considered here f_{O_2} and f_{H_2} are very nearly equal to their respective partial pressures, p_{O_2} and p_{H_2} , whereas $f_{\text{H}_2\text{O}}$ differs from $p_{\text{H}_2\text{O}}$ to some extent because the proportionality constant relating these two quantities, the fugacity coefficient, is of the order of 0.95 (Hol-

¹ This includes H_2O , H_2 , O_2 , SO_2 , S_2 , H_2S , CO_2 , CO , *etc.*, or molecules which under magmatic temperatures are in a gaseous state and under plutonic magmatic conditions are generally present in solution in the silicate melt. Heavy ions, such as Fe, Mg, Ca, *etc.*, have a finite, but very small, vapor pressure, and will be neglected as volatile constituents.

ser, 1954). However, because of the approximate nature of the calculations, the fugacities of all the volatiles will be taken equal to their respective partial pressures (see for comparison the calculation of Buddington and Lindsley, 1964, p. 320).

If it is *first assumed* that H_2O and its dissociation products H_2 and O_2 are the only volatiles present in the magma, then f_{O_2} at $1400^\circ K$ is found directly from the reaction (utilizing the equilibrium constants from Wagon *et al.*, 1945):

$$H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)} \quad (1)$$

$$K_{(1)}^{1400^\circ K} = \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{1/2}} = 10^{6.3}$$

but because $p_{H_2} = 2p_{O_2}$ and $p_{H_2O} = 500 \text{ bars} = 10^{2.7} \text{ bars}$

$$\frac{10^{2.7}}{2p_{O_2}^{3/2}} = 10^{6.3}$$

$$p_{O_2} = 10^{-2.6}$$

At $1200^\circ K$ ($927^\circ C$) and $f_{H_2O} = 1000 \text{ bars}$

$$p_{O_2} = 10^{-3.9}$$

Under such oxygen fugacities hematite would be the stable Fe-oxide (*cf.* Buddington and Lindsley, 1964).

Few plutonic rocks contain hematite as the Fe-oxide phase, most gabbroic rocks having ilmenite—magnetite assemblages, or ulvöspinel, either of which implies a much lower f_{O_2} . The first assumption that $p_{H_2} = 2p_{O_2}$ thus fails on mineralogical grounds; it is also inconsistent with the probable past history of the water in the magma, *i.e.* equilibrated for eons with high-temperature magmas and Fe-silicates, in which case it should have excess H_2 .

The assumption that H_2O , H_2 , and O_2 are the sole volatile constituents in a magma is again invalid on the basis of numerous studies of the gases evolved from active volcanoes. Eaton and Murata (1960), for example, list the average Hawaiian volcanic gases in volume percent as H_2O 79.31; H_2 0.58; CO_2 11.61; CO 0.37; SO_2 6.48; S_2 0.24. That the f_{O_2} in a magmatic system with these volatile constituents will be drastically different from the assumed case with only H_2 and H_2O present, has been emphasized by Verhoogen (1962b, p. 174) and, in a survey of chemical equilibrium in magmatic gases, by Ellis (1957). As an illustration one can take from Ellis (p. 420) data for a system approximating that of the Hawaiian volcanoes composed of H_2O - CO_2 - H_2 - S_2 in the molecular

ratio 100:10:2:1; mole fractions composed of volatile species at 1200°K and 1400°K are summarized in Table 8. Although the mole fractions at elevated p_{total} in this complex system were not calculated by Ellis, their approximate values may be inferred from high pressure values for a simpler system, also shown in Table 8. If, for a $f_{\text{H}_2\text{O}} = 1000$ bars and a temperature of 1200°K, $x_{\text{H}_2\text{O}}$ is taken as 900×10^{-3} and $x_{\text{H}_2\text{O}}$ as 4×10^{-3} , then p_{O_2} may be found approximately from the expression

$$p_{\text{O}_2} = \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \times K_{(1)}^{1200^\circ\text{K}}} \right)^2 \approx \left(\frac{9 \times 10^2}{4 \times 10^{7.9}} \right)^2 \approx 10^{-11} \text{ bars}$$

This value is not incompatible with that necessary for the formation and nonoxidation of ilmenite previously noted. This f_{O_2} , moreover, is about

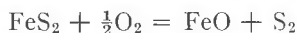
TABLE 8. MOLE FRACTIONS¹ ($\times 10^3$) OF GASES (after Ellis, 1957)

T°K	P (bars)	X _{H₂O}	X _{H₂S}	X _{SO₂}	X _{H₂}	X _{S₂}	X _{CO₂}	X _{CO}	X _{COs}
System H ₂ O-H ₂ -S ₂ , Molecular Ratio 100:2:1									
1400	1	938.8	5.3	13.9	41.9	0.080			
1200	1	957.9	11.7	7.5	22.8	0.105			
1200	1000	975.8	18.1	1.5	4.6	0.006			
System H ₂ O-CO ₂ -H ₂ -S ₂ , Molecular Ratio 100:10:2:1									
1400	1	859	4	14	34	0.005	81	8	0.02
1200	1	873	10	8	20	0.1	86	3	0.3

¹ The partial pressure of any volatile is the product of its mole fraction and P_{Total} .

the same as the inferred f_{O_2} in the Skaergaard gabbros at similar temperatures (Bartholomé, in Wager, *et al.*, 1957; Buddington and Lindsley, 1964, Table 1).

In the Skaergaard rather abundant sulfides are found throughout the intrusion whereas in the Guadalupe pyrite and pyrrhotite are limited to the most magnesian gabbros. Accordingly, in the Guadalupe reactions of the general type



must have proceeded to the right after the formation of the magnesian gabbros. The displacement from the equilibrium condition probably wasn't much, and may have been occasioned simply by decreasing temperature (see Holland, 1959). If f_{O_2} in the Guadalupe had been one or two

orders of magnitude less, sulfides might have appeared throughout more of the differentiation sequence.

In conclusion, it appears as though f_{O_2} in the Guadalupe magma was, at most, only a few orders of magnitude more than that in the Skaergaard. It is important to realize that geologically large variations in f_{H_2O} produce only very small variations in the equilibrium f_{O_2} . Variations in the magma in quantities of other volatiles which can participate in oxygen consuming or liberating reactions is of paramount significance.

VARIATIONS IN f_{O_2} AND f_{H_2O} AND THE TREND OF DIFFERENTIATION

Because the Guadalupe differentiation trend shows chemical and mineralogical similarities to the plutonic calc-alkaline trend (Best, 1963, Fig. 13 and pp. 253–257), it is important to make some comments on the role which the f_{O_2} and f_{H_2O} played in determining this trend of differentiation. Considerable current interest in fundamental principles of petrogenesis has been stimulated by the experimental discovery that variable f_{O_2} influences the course of crystallization of mafic magmas. Thus, both Kennedy (1955) and Osborn (1962) suggest that the “Bowen trend” of late enrichment in silica is occasioned by a relatively high f_{O_2} (or a constant f_{O_2} during crystallization) and the “Fenner trend” of Fe-enrichment by a low f_{O_2} (or total composition of system remains constant). The usual natural examples cited for these trends, respectively, are the common calc-alkaline suites of orogenic zones, consisting of gabbro-diorite-granodiorite-quartz monzonite or the extrusive sequence basalt-andesite-dacite-rhyolite, and the Skaergaard intrusion of gabbro-ferrogabbro-Fer-rich granophyre.

It has been shown that the f_{O_2} in the Guadalupe magma was not greatly more than that prevailing in the Skaergaard. If a relatively high (or constant) f_{O_2} did not prevail during crystallization and differentiation of the Guadalupe magma, the question arises as to whether it can be a factor generally in the development of the calc-alkaline trend. One significant characteristic of this trend, whether plutonic or volcanic, is the very common occurrence of hornblende and biotite, often to the exclusion of pyroxenes and olivine. Variations in f_{O_2} cannot alone promote the development of *hydrous* mafic silicates.

The suggestions of Kennedy (1955) and Osborn (1962) need to be critically evaluated by detailed chemical and mineralogical studies of *natural* igneous sequences so as to determine the real extent of variations in f_{O_2} in natural magmas (see Fudali, 1965, p. 1063). In this regard it should be noted that techniques are now available to evaluate, with varying degrees of accuracy, the intensive variables f_{O_2} , f_{H_2O} , and T in magmatic systems (Buddington and Lindsley, 1964; Wones and Eugster, 1965).

In the Guadalupe, f_{H_2O} was relatively high, sufficient to allow crystallization of hornblende, in even the earliest differentiates. If hornblende crystallizes to some extent in place of Ca-rich clinopyroxene, which is greatly dominant over Ca-poor pyroxene in both the Guadalupe and the Skaergaard, then the residual magma will be depleted in Fe and enriched in Si, relative to one in which hornblende does not form. The reason for this is the higher Fe and lower Si (relative to some datum, such as number of O atoms) in hornblende than in coexisting Ca-rich clinopyroxene. Early crystallization of biotite enhances this "hornblende effect." Thus it would seem that high values of f_{H_2O} , permitting early crystallization of hornblende, lead to Si-rich, Fe-poor late differentiates, as in the Guadalupe or the classic calc-alkaline trend, whereas low f_{H_2O} prohibits hornblende precipitation and leads to the Skaergaard trend of Fe-enrichment.

This hornblende effect cannot account for all the chemical and mineralogical aspects of the calc-alkaline trend, and it would be unreasonable to think it should. Other factors as well must be operative. For example, early crystallization of hornblende would deplete the residual magma in Na and K but this is hardly a property of calc-alkaline sequences. There seems to be some process whereby late granitic residua, enriched in Si, Na, and K, develop in conjunction with more mafic, early differentiates (gabbro or diorite), but with little or no bridging rock types. This is the situation in the Guadalupe complex.

SUMMARY AND CONCLUSIONS

An investigation of mineral compositions in the Guadalupe igneous complex provides information on mineral chemistry, phase relations in the crystallizing magma, partition of elements between coexisting phases, and the intensive variables f_{O_2} , f_{H_2O} , and T prevailing during crystallization. The complex bears many similarities to the plutonic calc-alkaline suite common to orogenic belts, and the data presented and discussed here should be considered in this context. The general field relations and petrology of the complex suggest it originated essentially by differentiation, *in situ*, of a parent basaltic magma.

Chemical and mineralogical data have established a new trend of pyroxene crystallization. It consists of coexisting clinopyroxene and orthopyroxene, lacks essential pigeonite, and has more extreme values of Ca than other well documented igneous trends, particularly the tholeiitic, low f_{H_2O} trend. The partition of Ca, Mg, and Fe^{2+} between the pyroxenes is essentially the same as in other calc-alkaline plutonic suites and bears similarities to that in high-grade regional metamorphic rocks. The Guadalupe pyroxenes crystallized at temperatures lower than in other

documented igneous bodies because of depression of the pyroxene liquidus well down on the solvus, owing to elevated $f_{\text{H}_2\text{O}}$ in the magma.

Because of the relatively high $f_{\text{H}_2\text{O}}$, hornblende appears early in the gabbroic differentiates, biotite appears in late gabbroic differentiates, and these two hydrous ferromagnesian mineral then take the place of pyroxenes throughout the more silicic, late differentiates. Hornblendes show Fe/Mg-enrichment relative to increasing Si in host rock, whereas biotite values rise and then fall. Experimental studies (Wones and Eugster, 1965) show that in Fe-bearing hydrous silicates either a Mg- or a Fe-enriched crystallization trend may develop, depending on the variations in f_{O_2} , $f_{\text{H}_2\text{O}}$, and T .

Fe-sulfides occur sparingly in the earliest gabbroic differentiates. Ilmenite is the dominant oxide phase in gabbroic rocks, although additional triangular-textured intergrowths of ilmenite-magnetite are found in some gabbros and typically in silicic differentiates.

The chemical composition of the ilmenites allows certain inferences to be drawn regarding the f_{O_2} during crystallization of the magma and cooling of the rocks. Utilizing experimental data of Buddington and Lindsley (1964) and Taylor (1964) on Ti-Fe-O equilibria, it appears that f_{O_2} must not have been greater than $10^{-10.5}$ to $10^{-13.5}$ bars during crystallization from 1100°C to 900°C. During subsequent cooling the f_{O_2} must have been approximately buffered in some manner.

A further evaluation of f_{O_2} in the magma can be made by approximate calculations on gas equilibria. f_{O_2} cannot be governed by equilibration with only H_2 and H_2O because very high values obtain, which would permit only hematite to crystallize as the stable oxide phase. A more realistic approach (see for example, Ellis, 1957) is to consider O_2 as participating in equilibria with several volatile constituents, such as S_2 , H_2S , SO_2 , CO_2 , H_2 , H_2O , in the magma. This approach yields f_{O_2} values close to those obtained from ilmenite compositional relations and, at most, only about two orders of magnitude more than those inferred for the Skaergaard magma. If these f_{O_2} values are reasonably accurate, then the two contrasting differentiation trends—the Skaergaard and the calc-alkaline—cannot be occasioned simply by variations in f_{O_2} , as suggested by Kennedy (1955) and Osborn (1962). Detailed mineralogical and chemical investigations of other *natural* igneous rock suites are needed to evaluate the intensive variables f_{O_2} , f_{H_2} , and T and their role in producing divergent trends of magmatic descent.

It is suggested that one relevant factor in the development of the calc-alkaline suite, as contrasted with, for example, the extreme Fe-enrichment of the Skaergaard, is relatively high $f_{\text{H}_2\text{O}}$ in the magma. This permits early and sustained crystallization of hornblende and biotite, both

of which serve to deplete the residual magma in Fe and enrich it in Si, relative to the situation in a "dry" magma crystallizing pyroxenes.

ACKNOWLEDGEMENTS

This study was made possible by generous assistance from many sources and individuals. To Mr. and Mrs. W. R. Wyre of Cathay Valley, California, I am indebted for continued hospitality whenever doing field work in the area. All of the mineral separations and most of the optical work was done while on the staff at the University of Ottawa (Canada), and the use of their equipment plus their generous help on various aspects of the laboratory work are gratefully acknowledged. Grants from the Geological Survey of Canada and the Geological Society of America defrayed the cost of chemical analyses. George Chao very kindly took numerous single crystal X-ray photographs which aided in the interpretation of the exsolution lamellae in clinopyroxenes. Thanks are due the staff in the Department of Geology, Pomona College, for their assistance in the use of the electron microprobe analyzer. George Turner kindly supplied unpublished optical data on pyroxenes from the Bucks Lakes pluton, California. Sherman Grommé made available his own observations on the oxide phases in the gabbroic rocks. Considerable benefit to the discussion of exsolution in pyroxenes was gained through exchange of ideas and data with John M. Moore and with Ray A. Binns, who also pointed out the textural similarity of some of the gabbroic rocks with granulite facies metamorphic rocks and the possibility of autometamorphism; the section on ilmenites and f_{O_2} benefited from the comments of Donald H. Lindsley. For critical reading of the entire manuscript, I am indebted to W. Revell Phillips, Ray A. Binns, and Edward L. P. Mercy.

REFERENCES

- BARTHOLOMÉ, P. (1962) Iron-magnesium ratio in associated pyroxenes and olivines. *Geol. Soc. Amer. Buddington Vol.*, 1-20.
- BEST, M. G. (1963) Petrology of the Guadalupe igneous complex, southwestern Sierra Nevada foothills, California. *J. Petrology* **4**, 223-259.
- BINNS, R. A. (1962) Metamorphic pyroxenes from the Broken Hill district, New South Wales. *Mineral. Mag.* **33**, 320-338.
- (1964) Zones of progressive regional metamorphism in the Willyama complex, Broken Hill District, New South Wales. *J. Geol. Soc. So. Aust.* **11**, 283-330.
- , J. V. P. LONG, AND S. J. B. REED (1963) Naturally occurring members of the clinostatite-clinoferrrosilite mineral series. *Nature* **198**, 777-778.
- BOESEN, R. S. (1964) The clinopyroxenes of a monzonitic complex at Mount Dromedary, New South Wales. *Amer. Mineral.* **49**, 1435-1457.
- BOWN, M. G. (1964) Recalculation of pyroxene analyses. *Amer. Mineral.* **49**, 190-194.
- AND P. GAY (1959) Identification of oriented inclusions in pyroxene crystals. *Amer. Mineral.* **44**, 592-603.

- AND P. GAY. (1960) An X-ray study of exsolution phenomena in the Skaergaard pyroxenes. *Mineral. Mag.* **32**, 379–388.
- BOYD, F. R. AND J. F. SCHAIRER (1964) The system $MgSiO_2$ - $CaMgSi_2O_6$. *J. Petrology* **5**, 275–309.
- BRETT, P. R. (1962) Exsolution textures and rates in solid solution involving bornite. *Carnegie Inst. Wash. Year Book.* **61** 155–157.
- BROWN, G. M. (1957) Pyroxenes from the early and middle stages of fractionation of the Skaergaard intrusion, East Greenland. *Mineral. Mag.* **31**, 511–543.
- AND E. A. VINCENT (1963) Pyroxenes from the late stages of fractionation of the Skaergaard intrusion, East Greenland. *J. Petrology* **4**, 175–197.
- BUDDINGTON, A. F. AND D. H. LINDSLEY (1964) Iron-titanium oxide minerals and synthetic equivalents. *J. Petrology* **5**, 310–357.
- CARMICHAEL, I. S. E. (1960) The pyroxenes and olivines from some tertiary acid glasses. *J. Petrology* **1**, 309–336.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock-forming Minerals. Vol. 2: Chain Silicates, Vol. 3: Sheet Silicates, Vol. 5: Non-Silicates.* John Wiley and Sons, Inc., New York.
- AND D. ABBOT (1965) Clinopyroxenes of the gabbro cumulates of the Kap Edvard Holm complex, East Greenland. *Mineral. Mag.* Tilley Vol., 177–193.
- DE VORE, G. W. (1957) The association of strongly polarizing cations with weakly polarizing cations as a major influence in element distribution, mineral composition, and crystal growth. *J. Geol.* **65**, 178–195.
- EATON, M. P. AND K. J. MURATA (1960) How volcanoes grow. *Science* **132**, 925–938.
- ELLIS, A. J. (1957) Chemical equilibrium in magmatic gases. *Amer. J. Sci.* **255**, 416–431.
- FOSTER, M. D. (1960) Interpretation of the composition of trioctahedral micas. *U.S. Geol. Surv. Prof. Pap.* **354 B**, 1–49.
- FOX, P. E. (1966) *Petrology of Adamant Mountain Pluton, British Columbia.* PhD Thesis, Carleton University, Ottawa, Canada.
- FUDALI, R. F. (1965) Oxygen fugacities of basaltic and andesitic magmas. *Geochim. Cosmochim. Acta* **29**, 1063–1076.
- HEINRICH, E. W. (1946) Studies in the mica group: the biotite-phlogopite series. *Amer. J. Sci.* **244**, 836–848.
- HESS, J. J. (1949) Chemical composition and optical properties of common clinopyroxenes. *Amer. Mineral.* **34**, 621–666.
- (1960) Stillwater igneous complex. *Geol. Soc. Amer. Mem.* **80**.
- HOLLAND, J. D. (1959) Some applications of thermochemical data to problems of ore deposits. I. Stability relations among the oxides, sulfides, sulfates, and carbonates of ore and gangue metals. *Econ. Geol.* **54**, 184–233.
- HOLSER, W. T. (1954) Fugacity of water at high temperatures and pressures. *J. Phys. Chem.* **58**, 316–317.
- KENNEDY, G. C. (1955) Some aspects of the role of water in rock melts. *Geol. Soc. Amer. Spec. Pap.* **62**, 489–509.
- KRETZ, R. (1963) Distribution of magnesium and iron between orthopyroxene and calcic pyroxene in natural mineral assemblages. *J. Geol.* **71**, 773–785.
- LARSEN, F. S. AND W. M. DRAISIN (1950) Composition of the minerals in the rocks of the Southern California Batholith. *Int. Geol. Congr., 18th, Rep.*, **II**, 66–79.
- LE BAS, M. J. (1962) The role of aluminum in igneous clinopyroxenes with relation to their parentage. *Amer. J. Sci.* **260**, 267–288.
- LINDSLEY, D. H. (1965) Pseudobrookite series. *Carnegie Inst. Wash. Year Book* **64**, 146–148.

- MC DOUGALL, I. (1961) Optical and chemical studies of pyroxenes in a differentiated Tasmanian dolerite. *Amer. Mineral.* **46**, 661-687.
- MILLER, F. S. (1938) Hornblendes and primary structures of the San Marcos gabbro. *Geol. Soc. Amer. Bull.* **49**, 1213-1232.
- MUIR, I. D. (1954) Crystallization of pyroxenes in an iron-rich diabase from Minnesota. *Mineral. Mag.* **30**, 376-388.
- MURRAY, R. J. (1954) The clinopyroxenes of the Garbh Eilean sill, Shiant Isles. *Geol. Mag.* **91**, 17-31.
- NICKEL, E. H. (1954, 1955) The distribution of major and minor elements among some co-existing ferromagnesian silicates. *Amer. Mineral.* **39**, 486-493; **40**, 699-703.
- NOCKOLDS, S. R. AND R. L. MITCHELL (1948) The geochemistry of some Caledonian plutonic rocks: a study in the relationship between the major and trace elements of igneous rocks and their minerals. *Trans. Roy. Soc. Edinb.* **61**, 533-575.
- OSBORN, E. F. (1962) Reaction series for subalkaline igneous rocks based on different oxygen pressure conditions. *Amer. Mineral.* **47**, 211-226.
- PHILLIPS, R. (1963) The recalculation of amphibole analyses. *Mineral. Mag.* **33**, 701-711.
- AND LAYTON, W. (1964) The calciferous and alkali amphiboles. *Mineral. Mag.* **33**, 1097-1109.
- POLDERVAART, A. AND H. H. HESS (1951) Pyroxenes in the crystallization of basaltic magma. *J. Geol.* **59**, 472-489.
- ROEDDER, E. (1965) A laboratory reconnaissance of the liquidus surface in the pyroxene system En-Di-Hd-Fs (MgSiO_2 - $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ - FeSiO_3). *Amer. Mineral.* **50**, 696-703.
- SAHAMA, T. G. (1960) Kalsilite in the lavas of Mt. Nyiragongo (Belgian Congo). *J. Petrology* **1**, 146-171.
- SUBRAMANIAM, A. P. (1962) Pyroxenes and garnets from charnockites and associated granulites. *Geol. Soc. Amer.*, Buddington Vol., 21-36.
- TAYLOR, R. W. (1964) Phase equilibria in the system FeO - Fe_2O_3 - TiO_2 at 1300°C. *Amer. Mineral.* **49**, 1016-1030.
- VERHOOGEN, J. (1962a) Distribution of titanium between silicates and oxides in igneous rocks. *Amer. J. Sci.* **260**, 211-220.
- (1962b) Oxidation of iron-titanium oxides in igneous rocks. *J. Geol.* **70**, 168-181.
- VINCENT, E. A. AND R. PHILLIPS (1954) Iron-titanium oxide minerals in the layered gabbros of the Skaergaard intrusion, East Greenland. Part I: *Geochim. Cosmochim. Acta* **6**, 1-26.
- WAGER, L. R., E. A. VINCENT, AND A. A. SMALES (1957) Sulphides in the Skaergaard intrusion, East Greenland, with an appendix by P. Bartholomé. *Econ. Geol.* **52**, 855-904.
- WAGMAN, D. D., J. E. KILPATRICK, W. J. TAYLOR, K. S. PITZER, AND F. D. ROSSINI (1945) Heats, free energies, and equilibrium constants of some reactions involving O_2 , H_2 , H_2O , C, CO, CO_2 , and CH_4 . *J. Res. Nat. Bur. Stand.* **34**, 143-162.
- WILKINSON, J. F. G. (1956) Clinopyroxenes of alkali olivine-basalt magma. *Amer. Mineral.* **41**, 724-743.
- WONES, D. R. AND H. P. EUGSTER (1965) Stability of biotite: experiment, theory and application. *Amer. Mineral.* **50**, 1228-1272.
- YODER, H. S., JR. AND C. E. TILLEY (1962) Origin of basalt magmas: an experimental study of natural and synthetic rock systems. *J. Petrology* **3**, 342-532.
- , C. E. TILLEY, AND J. F. SCHAIRER (1964) Isothermal sections of pyroxene quadrilateral. *Carnegie Inst. Wash. Year Book* **63**, 121-129.