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## HALOGEN CONTENTS OF IGNEOUS MINERALS AS INDICATORS OF MAGMATIC EVOLUTION OF ROCKS ASSOCIATED WITH THE RAY PORPHYRY COPPER DEPOSIT, ARIZONA

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**Abstract.**—The contents of Cl, F, and H<sub>2</sub>O+ (calculated) in some hydrous igneous minerals in intrusive rocks of Laramide age (70–80 m.y.) near Ray, Ariz., appear to be related to the age and the chemistry of the whole-rock samples. Apatite and biotite in younger, more silicic rocks contain more F but less Cl and H<sub>2</sub>O+ than apatite and biotite in older, more mafic rock; the same relations hold for F and H<sub>2</sub>O+ in sphene. Correlations of the abundance of Cl, F, and H<sub>2</sub>O+ in hornblende with rock chemistry and age are not as strong as for apatite, biotite, and sphene; igneous(?) epidote does not contain Cl and F in amounts detectable by electron microprobe analysis. The contents of Cl, F, and H<sub>2</sub>O+ in whole-rock samples decrease with increasing differentiation index and decreasing age. Data for a single pluton of variable composition mirror the results for a suite of different plutons and dikes. The data are satisfactorily although not exclusively explained by postulating that the melts each contained progressively less Cl, F, and H<sub>2</sub>O and that the hydrous minerals consumed most of the Cl, F, and H<sub>2</sub>O in the magmas. The data may also be explained by postulating that (1) the stocks evolved Cl-bearing water during their ascent and crystallization, or that (2) Cl and H<sub>2</sub>O were concentrated during differentiation of the stocks but the minerals failed to record their buildup. Both alternative explanations and problems with and require special conditions to satisfy field, chemical, and experimental data. If many of the special conditions are not met, a nearby batholithic parent to the stocks is not a favorable source of the mineralized fluids at Ray. Propylitic alteration of biotite results in Cl-poor chlorites and may have provided some Cl to hydrothermal fluids; biotite may have also supplied some F to propylitizing fluids through alteration.

This study provides data on the concentrations of Cl, F, and H<sub>2</sub>O in the intrusive bodies and their hydrous minerals related in time and space with the porphyry copper deposit at Ray, Ariz. These and accompanying whole-rock petrochemical data allow interpretation of the magmatic behavior of Cl, F, and H<sub>2</sub>O prior to deposition of ore. Microprobe and wet-chemistry analyses for Cl, F, and H<sub>2</sub>O+ of mineral grains and whole-rock samples of least altered Laramide intrusive rocks, of mineral grains in least altered Precambrian igneous

rocks (Ruin Granite, 1.4 b.y.; diabase, 1.2 b.y.), and of hydrothermal biotite from the deposit are reported. The igneous minerals studied are apatite, biotite, hornblende, sphene, and epidote; secondary minerals include chlorite, epidote, sphene, phengite, and hydrogarnet(?).

The samples used in the microprobe studies were collected at sites indicated in figure 1 and include 7 of at least 12 rock types intruded in the vicinity of the Ray deposit during a 10-m.y. period (70–60 m.y. ago; Banks and others, 1972; Banks and Stuckless, 1973). Ages, differentiation indices, textures, the Fe-Mg silicates present, and percentage of alteration of selected minerals in the Laramide igneous rocks are listed in table 1. Whole-rock chemical and petrologic data have been obtained on one or more samples of each of the 12 rock types. At least 11 of these rock types are cut by sulfide veins; part of this veining occurs outside of presently commercial ground.

The deposit, located about 120 km north of Tucson and 120 km east of Phoenix, Ariz. formed about 60 m.y. ago (Banks and Stuckless, 1973). The main hosts of the hypogene sulfides (pyrite, chalcopyrite, and molybdenite) are schist, Ruin Granite (a quartz monzonite), quartzite, and diabase, all of Precambrian age. The center of mineralization occurs near the west-central edge of the Sonora quadrangle (fig. 1).

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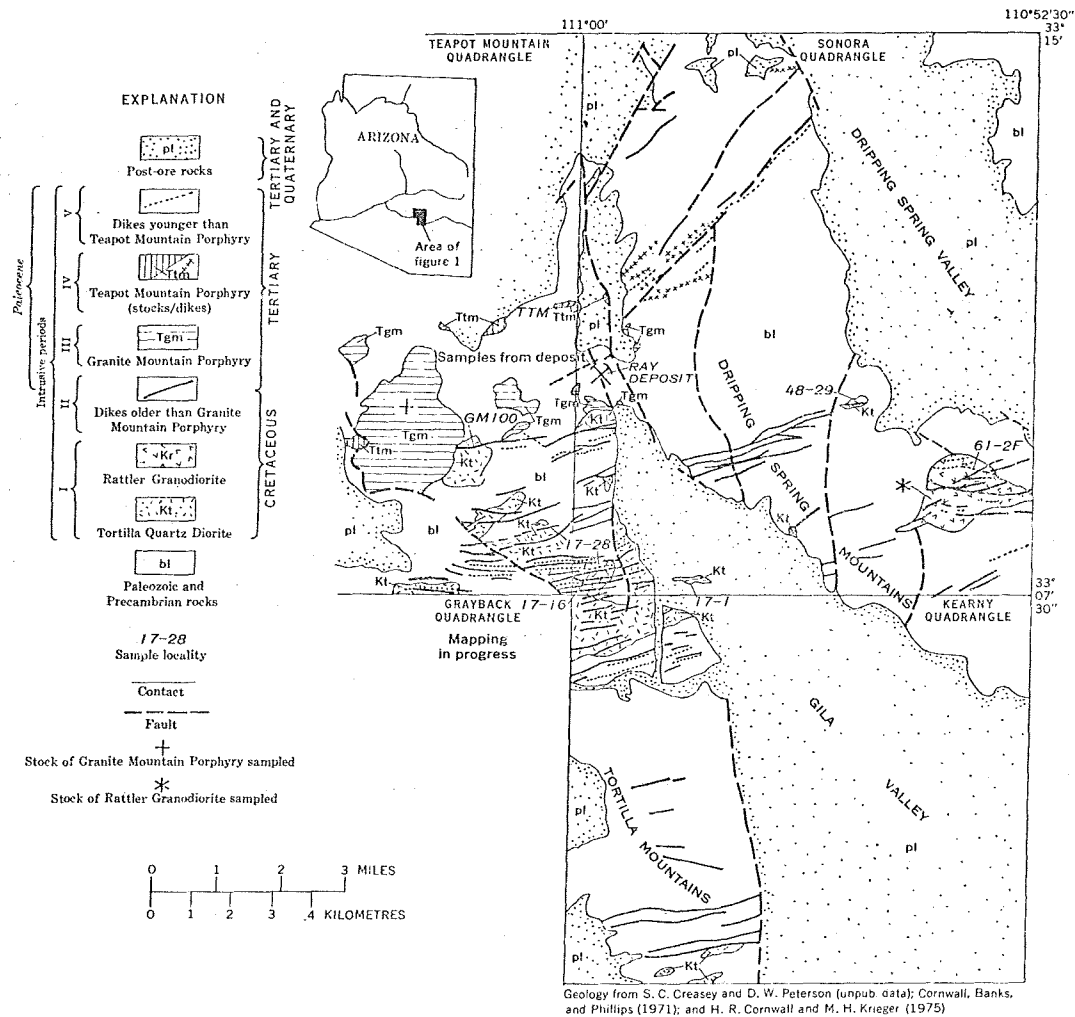


FIGURE 1.—General geology and sample locations.

#### BACKGROUND GEOLOGY AND PETROLOGY OF LARAMIDE IGNEOUS ROCKS

Laramide igneous bodies near Ray were intruded in roughly five periods (fig. 1) that may or may not represent a nearly continuous sequence. One or more major plutons, representing five rock types, were emplaced during each of the first four intrusive periods. The samples for microprobe study came from four of these five major rock types. The excepted rock type represents a granodiorite stock of intrusive period II (63

m.y. old) in the Grayback quadrangle (not shown in fig. 1). Rhyodacitic to quartz latitic dikes were emplaced in intrusive periods II, IV, and V. Samples of the dikes for microprobe study came from two rock types of period II (samples 17-16 and GM100, table 1) and one type of period V (sample 61-2F, table 1).

Bulk compositions of the major Laramide plutons are progressively more felsic (increasing differentiation index) with decreasing age of the intrusive type; these ages were determined on the basis of geologic

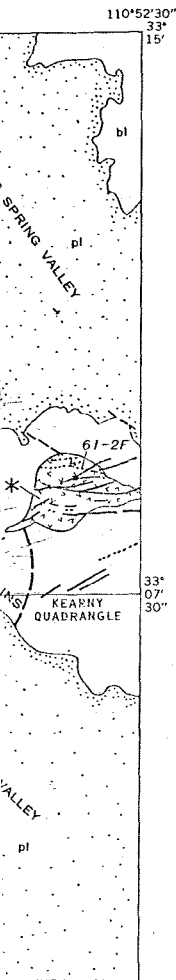


TABLE 1.—Sample data, Laramide rocks

Rock sample <sup>1</sup>	Rock differentiation index <sup>2</sup>	Texture	Mafic silicates present			Percentage of mafic minerals altered <sup>3</sup>	Percentage of plagioclase altered <sup>4</sup>
			Pyroxene	Hornblende	Biotite		
<b>Tortilla Quartz Diorite (71-70 m.y.)<sup>5</sup></b>							
17-28	51.4	Intersertal	X	X	X	Trace	16.0
17-1	51.9	do	X	(*)	X	19.5	5.0
48-29	53.2	do	X	X	--	10.0	45.0
<b>Rattler Granodiorite (70 m.y.)</b>							
46-99B	48.4	Hypidiomorphic-seriate	X	X	X	1.3	6.6
60-113D†	64.7	Porphyritic	--	X	X	11.3	3.8
60-108	72.3	Hypidiomorphic-seriate	Trace	X	--	Trace	1.0
60-114†*	72.2	Porphyritic	--	X	X	2.4	3.0
61-25†	72.4	do	--	X	X	8.2	3.5
60-91	72.5	Seriate porphyritic	--	X	X	11.0	11.2
60-111	72.7	Chilled	--	X	X	2.0	0.6
60-124*	72.8	Hypidiomorphic-seriate	--	X	X	13.3	10.0
60-98	75.2	do	--	X	X	1.7	3.6
40-11G	75.4	do	--	X	X	9.6	10.5
60-131	76.4	Seriate porphyritic	--	--	X	8.3	7.1
60-130	76.9	Hypidiomorphic-seriate	--	--	X	9.0	6.3
60-132*	77.1	do	--	--	X	17.7	7.1
60-96A	87.3	Aplitic	--	--	X	72.5	26.7
46-11A	93.3	do	--	--	X	72.2	35.9
T16-630†	71.5	Seriate porphyritic	--	X	X	--	--
<b>Granite Mountain Porphyry (61-60 m.y.)</b>							
RB5	79.7	Granitoid	--	--	X	46.0	39.5
GM14	80.5	Seriate porphyritic	--	--	X	12.5	12.1
GM12	81.8	Porphyritic	--	--	X	13.6	11.3
GM18	81.9	Granitoid	--	Trace	X	5.7	9.0
GM6G	83.5	Seriate porphyritic	--	do	X	9.2	2.3
GM1A	84.7	Aplitic	--	--	X	100.0	41.0
GM2A	84.7	do	--	--	X	85.7	21.0
GM4V	--	Porphyritic	--	--	X	16.7	2.5
<b>Teapot Mountain Porphyry (61-60 m.y.)</b>							
Ttm†	83.0	Porphyritic	--	X	X	100.0	68.0
<b>Rhyodacite dikes<sup>6</sup></b>							
17-16†	*74.0	Porphyritic	--	X	X	43.2	58.8
GM100†	*80.0	do	--	X	X	42.0	52.3
61-2F†	81.0	do	--	X	X	86.3	7.8

† Samples with phenocrystic magnetite and hydrous phases.  
 \* No mineral analyses.  
 † No modal analyses.  
 ‡ A numeral 2 or 3 preceding the sample numbers in the following tables indicates that the probe mount is a duplicate or triplicate sample.  
 § Modified from Thornton and Tuttle (1960): uses quartz plus albite plus K-feldspar from molecular cationorm rather than the CIPW norm.  
 ¶ Percentage of the Mg-Fe minerals in the rock converted to secondary minerals.  
 †† Percentage of the plagioclase in the rock converted to secondary minerals.  
 ‡‡ Ages from Banks and Stuckless (1973); Banks and others (1972).  
 §§ Fibrous amphibole reaction rims on pyroxene.  
 ¶¶ Aplite assumed to have approximately same differentiation index as sample GM2A.  
 ††† Ages as follows: Sample 17-16 (<69, >63 m.y.); sample GM 100 (63 m.y.); sample 61-2F (questionable, either 70 m.y. or <60 m.y.).  
 †††† Rock analysis from the same dike type but not the same dike used for the mineral analyses.

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relations and potassium-argon and fission-track ages (table 1). Compositions of the dike rocks are not all intermediate between those of rock types that they crosscut and that crosscut them. However, standard petrochemical plots of whole-rock normative minerals, major elements, and trace elements indicate that the magmas of both the dikes and the stocks of Laramide age near Ray developed along smooth chemical trends (Banks and others, 1972). The results are compatible with, although not proof of, either consanguinity or a common-source partial melting origin of the igneous suite. Various facies of the Rattler Granodiorite al-

most duplicate in one intrusive mass the chemical, textural and mineralogical variations that occur in the entire suite studied (table 1). This allows comparison of the behaviors of Cl, F, and H<sub>2</sub>O in one magma with their behaviors in a series of magmas intruded in the 10-m.y. period. Stratigraphic reconstructions indicate that during Laramide time the presently exposed rocks were at depths ranging from not more than 1.5 km to at least 3 km. Concordance of apatite fission-track ages with other mineral ages places a maximum depth for the exposed rocks and deposit at 5 km during and since Laramide time (Banks and Stuckless, 1973). Depths of

emplacement of the individual plutons studied may have differed by 1.5 km or more.

Several petrochemical observations suggest, although admittedly do not prove, that the stocks and dikes did not saturate early in their crystallization history or evolve much water. The Mg content of the biotite decreases slightly with increasing differentiation index of the sample and, more strikingly, with decreasing sample age (fig. 2). This reducing trend may represent undersaturation of the melt in regard to water (Wones and Eugster, 1965). Additionally, (1) the percentage of aplites in the stocks is low; (2) there is a paucity of pegmatitic aplites; (3) metamorphic aureoles around the intrusive bodies, both stocks and dikes, are very restricted and in some places are virtually absent even in carbonate terrane; (4) miarolitic features or cavities have not been identified in field exposures or thin sections of the Laramide stocks; and (5) J. T. Nash (written commun., 1971, 1972) and M. J. Logsdon (oral commun., 1973) find that the fluid inclusions in quartz in the rocks are sparse, two phase, relatively dilute, and homogenize at temperatures below 450°C.

Another petrologic observation that might indicate the degree of saturation of the magmas at their emplacement is the amount of melt crystallized prior to the first formation of the hydrous minerals. For example, at their depths of emplacement, the melts should have contained about 2.5–3.0 wt percent H<sub>2</sub>O before

biotite formed (D. R. Wones, oral commun., 1973; Wones and Dodge, 1966). Thus, if biotite first formed in a stock when it was 50 percent crystallized, the magma presumably had less than 1.5 wt percent initial H<sub>2</sub>O. However, as described below, not only is it difficult to determine with surety when the hydrous minerals first began forming in the magmas, but also the petrologic relations can be interpreted to indicate that a given mineral began forming at different times in the same magma.

In the porphyritic variants of the Rattler Granodiorite and in the rhyodacite dikes and Teapot Mountain Porphyry (flagged by daggers in table 1), anhedral (fig. 3A) to euhedral (fig. 3B) phenocrysts of hornblende, biotite, and anhydrous minerals are set in either an aplitic or felty groundmass composed mainly of quartz, K-feldspar, and, in some samples, also plagioclase, opaque minerals, hornblende, or biotite. Accessory apatite occurs as subhedral to euhedral grains and as inclusions, mostly in biotite. Sphene rims magnetite phenocrysts, is intergrown with biotite and hornblende, or locally is found as separate, subhedral to anhedral medium-sized grains. Provided that growth rate of the hydrous minerals did not greatly exceed the growth rate of the anhydrous minerals, these relations suggest that the hydrous minerals began forming in the magma before the groundmass, which makes up 30–50 percent of the rocks in this group of samples. However, in the other samples of the Rattler Granodiorite (not flagged by daggers in table 1) and in all samples of the Tortilla Quartz Diorite and Granite Mountain Porphyry (including porphyritic varieties), the hydrous minerals are interstitial to plagioclase (forming roughly 50 percent of the rocks) and are spatially associated with interstitial aplitic to oikocrystic K-feldspar and quartz (fig. 3D–H; fig. 4A). In the more felsic samples of this group, some of the larger K-feldspar and quartz grains (perhaps another 20–30 percent of the rocks) formed with the plagioclase and therefore also predate the hydrous minerals. Hornblende, biotite, and sphene display euhedral faces against each other and interstitial quartz or K-feldspar (fig. 4A, F), but they only rarely are euhedral against plagioclase. These relations indicate that at least the outer parts of the hydrous mineral grains are coeval with the interstitial quartz and K-feldspar and postdate main-stage growth of plagioclase and some quartz and K-feldspar but do not rule out the possibility that the cores of the grains began forming during plagioclase growth. Rare small inclusions of apatite, biotite, and hornblende in the early plagioclase might suggest the second possibility but might also be interpreted to be replacement features associated with fractures and crystal dislocations lo-

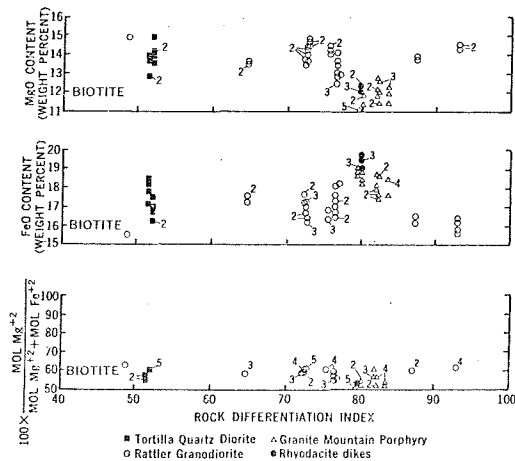


FIGURE 2.—Variation of MgO, FeO, and  $\frac{100 \times \text{mol Mg}^{2+}}{\text{mol Mg}^{2+} + \text{mol Fe}^{2+}}$  in biotite with rock differentiation index. All Fe in biotite is assumed to be in the reduced state for plotting.

commun., 1973; biotite first formed and crystallized, the wt percent initial not only is it difficult hydrous minerals, but also the and to indicate that different times in the

Rattler Granite-Teapot Mountain (table 1), anhedral microcrysts of hornblende and biotite are set in a groundmass composed mainly of plagioclase and quartz. Hornblende rims magnetite and hornblende, and biotite growth rate of hornblende exceed the growth rate of biotite. These relations suggest that the magma cooled up 30-50 percent. However, in the biotite (not flagged) samples of the Teapot Mountain Porphyry the hydrous mineral forming roughly 50 percent associated with quartz and biotite. In felsic samples of this and quartz grains (see rocks) formed to predate the hydrous sphenes display and interstitial biotite they only rarely show relations indicating hydrous mineral and K-feldspar growth of plagioclase but do not rule out the grains began to form small inclusions in the early stage possibility but cementation features and dislocations lo-

cated outside of the thin sections. Alternatively, rather than indicating favorable conditions for hydrous minerals throughout the magma, the small inclusions might have resulted from local concentrations of the required components that were rejected by the growing anhydrous plagioclase.

Although these petrographic relations suggest that the hydrous minerals may have formed earlier in some magmas or parts of magmas than in others, textural relations indicate that these minerals continued to form late during crystallization in both sample groups. Some hornblende and biotite in the first sample group include aplitic groundmass material in their edges (fig. 3A, B) and some in their centers, indicating, as does the presence of hydrous minerals in the groundmass (fig. 3C), that at least part of the growth of the hydrous minerals accompanied crystallization of the groundmass. In the samples of the second group, the hydrous minerals show crosscutting, interstitial, and coeval relations with the interstitial anhydrous minerals (fig. 4B, C) and replace the early-formed plagioclase (fig. 4D) and, in the more mafic samples, also pyroxene (fig. 4E). These relations and the presence of biotite, apatite, and sphene in the late-stage aplitic differentiates of all the stocks indicate that hydrous phases continued to form until only a small amount of liquid remained. All the hydrous minerals become less abundant with increasing differentiation index of the sample (fig. 5), and the modal amount of a given hydrous mineral is not detectably different when samples of like whole-rock composition from the two sample groups are compared.

Paragenetic relations between the different hydrous phases appear to vary somewhat with rock chemistry. In the more mafic samples, at least part of the hornblende appears intergrown with biotite, whereas in the more felsic Granite Mountain Porphyry, the hornblende occurs only as very rare needles (for example, sample GM18, tables 1, 5) in quartz that may predate biotite. Sphene in the mafic samples is interstitial to hornblende and biotite but in more felsic rocks appears coeval with these minerals (fig. 4F). For the most part, however, the frequency of mutual inclusion, intergrowth, replacement, and proximity coupled with similar physical relations with precursor and coeval anhydrous phases indicate that the formation of biotite, hornblende, apatite, and sphene was largely coeval (figs. 3D, H; 4D-F). Rare grains of interstitial epidote thought to be igneous or to be replaced interstitial glass are the exception and appear always to postdate the other hydrous phases, except perhaps sphene in the mafic samples. The epidote is sometimes chemically distinguishable from epidote formed at the expense of

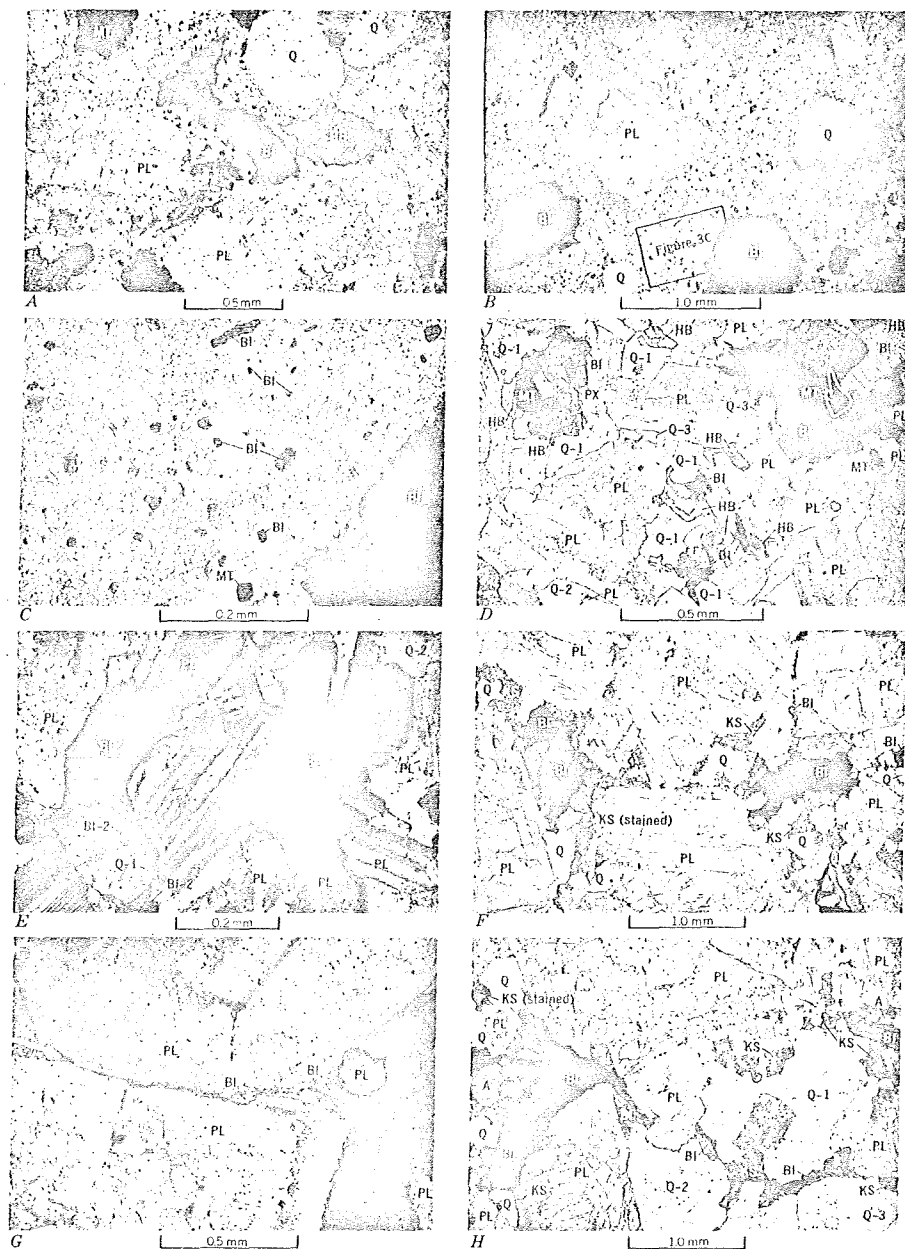
biotite and plagioclase in the same thin section, and igneous minerals in contact with it appear unaltered (fig. 4G, I). Compared to the other hydrous minerals, apatite is commonly euhedral (fig. 4D, E; 3H) and seems not to include apparently coeval hydrous, anhydrous silicate (it does include zircon and opaque minerals) or even plagioclase in occurrences where it appears to replace that mineral.

Crystal growth relations of the interstitial hydrous minerals, quartz, and K-feldspar appear to be complex. A given hydrous mineral grain may have a euhedral face in contact with an interstitial grain of a given anhydrous mineral, whereas the other face or other grain of the hydrous mineral in the same or different thin section of the same pluton may replace the K-feldspar and quartz or be intergrown with them (fig. 4A). The same relations occur between different hydrous minerals and also between interstitial quartz and K-feldspar. Also, replacement and overgrowth features occur between like-mineral grains. These relations indicate that the conditions governing mineral stabilities fluctuated repeatedly over short distances during formation of the interstitial material. They may also suggest equilibrium crystallization where continual reconstitution of the crucial components for growth of a given phase (among them Cl, F and H<sub>2</sub>O) was caused by rejection of the components by other nearby phases.

## ANALYTICAL RESULTS

### Methods

The mineral analyses were done with an ARL (Applied Research Lab.) model EMX-SM electron microprobe using an ADP crystal for Cl and an RAP crystal for F, an excitation voltage of 15 kV, sample currents of  $2.5 \times 10^{-8}$  or  $3 \times 10^{-8}$  A on brass, integration times (terminated on a fixed beam current) of about 40 s, and scapolite (2.57 wt percent Cl) and fluorapatite (3.83 wt percent F) as standards. The electron beam was fully focused. Buildup of carbon contamination and noticeable loss of volatile components were avoided by moving the beam with magnetic deflectors to sweep areas about 4-10  $\mu\text{m}^2$ . At the termination of each counting interval, the sample was moved under the beam about 1  $\mu\text{m}$ . If the grain shape and size did not allow this type of analysis, the sample was moved manually under a fully focused or defocused (2-3  $\mu\text{m}$ ) beam about every 10 s. The X-ray intensity data (counts), obtained by averaging 4-10 (usually 8) observations per analysis, were corrected by computer. Except for apatite, observation points were distributed over an area of about  $10 \times 10 \mu\text{m}$ . Data collection for apatite was similar to the above except that the data points



were distributed in two ways: (1) Equal numbers at centers and edges of the grain, or (2) as steps across a grain. Computer corrections included drift, back-

ground, and matrix corrections (mass absorption, secondary fluorescence, and atomic number effects: Besson, 1967; Beaman and Isasi, 1970). Major-element

data used in the computer corrections were gathered during 6-15 counting intervals (of about 20 s each) using (where appropriate) biotite, apatite, rhodonite, hornblende, rutile, hematite, orthoclase and plagioclase as standards.

Precision of the microprobe analyses is considered to be about  $\pm 10$  percent of the amount present for F and slightly better for Cl. Detection levels were established at three times the square root of the background counts (Birks, 1963). The average Cl and F contents of biotite in one sample determined by microprobe analysis agree within 17 percent of the amount determined by wet-chemical analysis (sample 261-25, table 4). This is good agreement considering the inhomogeneity of this sample with respect to Cl and F and considering the correction factors involved in using seapolite and apatite for Cl and F analysis of biotite. The values of  $H_2O+$  reported in tables 2-6 are calculated by difference by assuming ideality for each mineral phase and using the computer program of Jackson and others (1967) to obtain the required normalizing factors. The  $H_2O+$  data are less precise than the Cl and F data because the precision of the normalizing factor is influenced by sample homogeneity of six to nine elements rather than one. This and the variation in the major-element contents between mineral grains resulted in different calculated  $H_2O+$  contents for some of the mineral grains in tables 3-6, although the grains have similar Cl and F contents. The  $H_2O+$  content, by analysis, of one biotite (grain CHEM, sample 261-25,

table 4) is lower than that obtained by calculation and thus also is less than that required for ideality. It is not known whether this is real or resulted from excessively high temperatures used in drying the separate.

Supplementary analyses of whole-rock Cl, F, and  $H_2O+$  were done by wet-chemical methods. The Cl and F analyses were done on dry-rock powders and their water-leached splits. The water leaching removes Cl contributed by salts precipitated on fractures by ground water. The modal data were determined by combined observations of thin sections and stained rock slabs so that the effects of porphyritic texture and large grain size were minimized.

#### Comparative Cl, F, and $H_2O+$ contents of the minerals

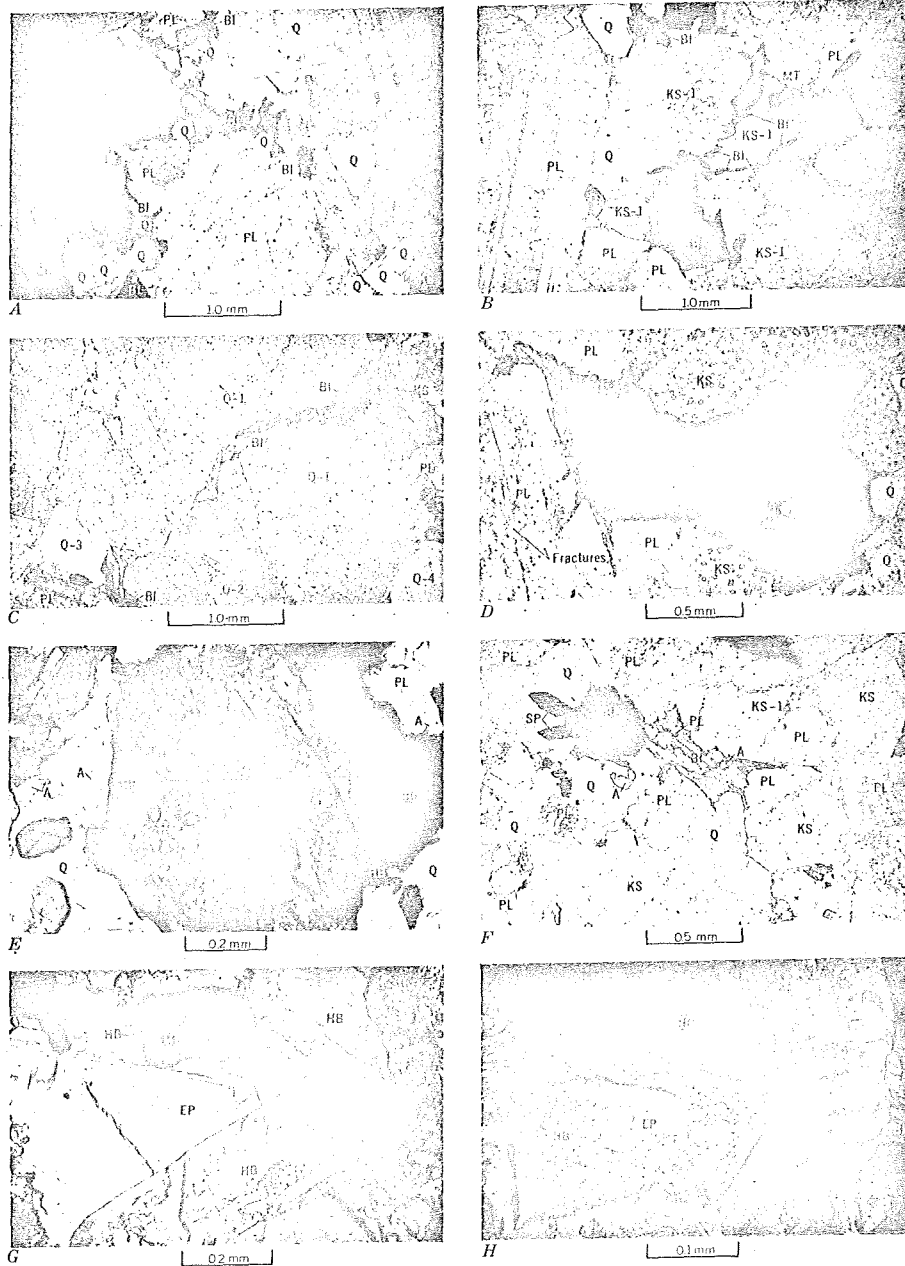
The Cl, F, and  $H_2O+$  contents of the minerals are summarized in table 2 and presented separately in tables 3-9. Cl and F generally show a preference for apatite over coexisting biotite, hornblende, sphene, and epidote (see also Stormer and Carmichael, 1971), whereas  $H_2O+$  shows a preference for the silicates over apatite. F is dominant over Cl in all the igneous minerals (see also Stormer and Carmichael, 1971, and Taborszky, 1962).

Biotite contains more  $H_2O+$  and F, and usually more Cl by weight than coexisting hornblende, sphene, and interstitial epidote. Correns (1956) and Gillberg (1964) found similar relations between the halogen contents of coexisting biotite and hornblende, and the data of Dodge and others (1968, 1969) for rocks of the Sierra Nevada batholith and Dodge and Ross (1971) for granitic rocks in the Coast and Transverse Ranges, Calif., show that coexisting biotite contains more  $H_2O+$  and F by weight and slightly less or the same amount of Cl than coexisting hornblende. Hornblende, like biotite, generally contains more Cl, F, and  $H_2O+$  by weight than coexisting sphene, whereas sphene contains less  $H_2O+$  and more F than interstitial epidote. In terms of atomic percent, biotite in a given sample contains  $Cl^-$ ,  $F^-$ , and  $OH^-$  in about the same relative proportions as hornblende and sphene (ranging from 0 to 2 percent for  $Cl^-$ , from 2 to 14 percent for  $F^-$ , and from 86 to 96 percent for  $OH^-$ ) but contains less  $Cl^-$  and  $F^-$  than apatite (ranging from 0 to 20 percent  $Cl^-$ , 32 to 98 percent  $F^-$ , and 2 to 48 percent  $OH^-$  apatite).

Hydrothermal biotite contains significantly different amounts of Cl and F compared with igneous biotite in equivalent rocks from outside the Ray deposit (table 2; in table 4 compare T123 with samples of Granite Mountain Porphyry). In addition to differences in Cl and F contents, hydrothermal biotite from Granite

FIGURE 3.—Textural relations of minerals in Laramide rocks at Ray, Ariz. (A, apatite; BI, biotite; KS, K-feldspar; HB, hornblende; MT, magnetite; PL, plagioclase; Q, quartz. Numbers indicate different outcrops of individual, optically continuous grains.) A, Sample 60-114, porphyritic facies of Rattler Granodiorite. Phenocrysts of euhedral to subhedral plagioclase, subhedral to anhedral quartz and magnetite, and anhedral biotite and hornblende in groundmass of plagioclase, K-feldspar, quartz, and biotite. B, Sample 61-25, porphyritic facies of Rattler Granodiorite. Phenocrysts of subhedral to euhedral plagioclase, biotite, hornblende (not shown), and magnetite and rounded quartz in groundmass of plagioclase, K-feldspar, biotite, and magnetite. C, Inset of figure 3B showing biotite in groundmass. D, Sample 17-28, Tortilla Quartz Diorite. Subhedral plagioclase with interstitial hornblende, biotite, and quartz. E, Sample 17-28, Tortilla Quartz Diorite. Detail of interstitial biotite and quartz. F, Sample 60-131, seriate porphyritic facies of Rattler Granodiorite. Quartz, K-feldspar (stained) and biotite interstitial to euhedral to subhedral plagioclase. G, Sample RB-5, Granite Mountain Porphyry. Euhedral plagioclase with biotite and interstitial oikocrystic K-feldspar (stained). H, Sample 60-131, seriate porphyritic facies of Rattler Granodiorite. Euhedral apatite and anhedral biotite, quartz, and K-feldspar (stained) interstitial to euhedral to subhedral plagioclase.

s absorption, secondary effects: Bee-  
) Major-element



Mountain Porphyry differs from igneous biotite by containing more Mg (66 versus 55 mole fraction

phlogopite). Roegge and others (1974) found approximately the same amount of Cl (0.07-0.09 wt percent)



as that of sample T123 in another sample of hydrothermal biotite from the Granite Mountain Porphyry at Ray.

The F content of the chlorite in the Laramide rocks correlates with greater than 99-percent confidence with the F content of its biotite precursor. Similarly, both biotite and its derivative chlorite in the Ruin Granite contain more F than the biotite and chlorite in the Laramide rocks (table 2). Positive correlations also were found between the contents of the major and other minor elements in the chlorites and their precursor biotites from the Laramide rocks (Banks, 1974). There is no correlation between the contents of F in the epidote, sphene, and hydrogarnet (?) analyzed and the content of F in the host biotite.

Analyses of four phengites are given in table 8, although the results are not summarized in table 2. Two are alteration products of plagioclase, and two are alteration products of chlorite. Additionally, an intense-

ly altered area of plagioclase (2GM14, grain 4SPA) containing unidentified fine-grained clay minerals, too

FIGURE 4.—Textural relations of minerals in Laramide rocks at Ray, Ariz. (A, apatite; Bl, biotite; EP, epidote; HB, hornblende; KS, K-feldspar; MT, magnetite; PL, plagioclase; PX, pyroxene; SP, sphene; Q, quartz. Numbers indicate outcrops of individual, optically continuous grains.) A, Sample 60-130, hypidiomorphic-seriate facies of Rattler Granodiorite. Euhedral plagioclase, interstitial anhedral K-feldspar, and anhedral to euhedral quartz, and biotite. Note euhedral face of biotite against quartz at left side of photograph. B, Sample 60-130, same sample as 3A. Biotite cutting and interstitial to interstitial K-feldspar. C, Sample 60-132, hypidiomorphic-seriate facies of Rattler Granodiorite. Biotite cutting oikocrystic quartz. D, Sample RB5, Granite Mountain Porphyry. Biotite and K-feldspar (stained) interstitial to and replacing plagioclase. Apatite in biotite. E, Sample 17-28, Tortilla Quartz Diorite. Biotite and hornblende rimming pyroxene. Apatite in interstitial quartz. F, Sample, RB5, Granite Mountain Porphyry. Sphene, apatite, and biotite with interstitial quartz and K-feldspar. G, H, Sample 4S-29, Tortilla Quartz Diorite. Epidote interstitial to unaltered hornblende and plagioclase.

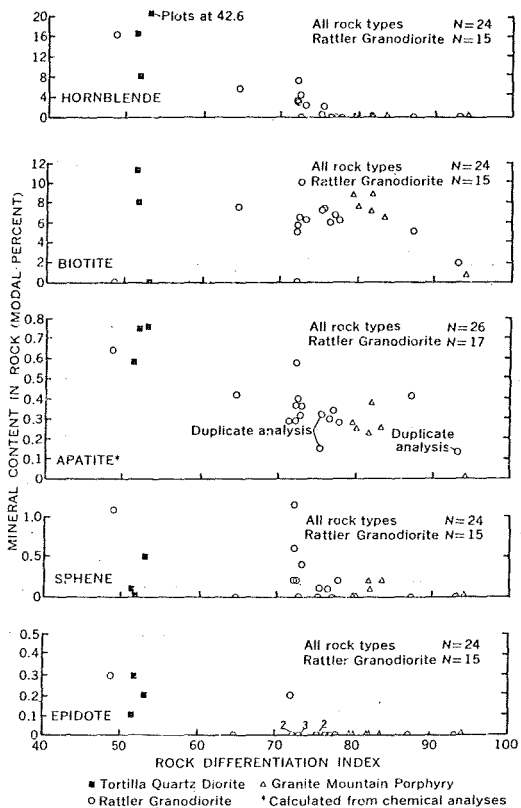


FIGURE 5.—Variation of mineral modal abundance with rock differentiation index.

TABLE 2.—Ranges of Cl, F, and H<sub>2</sub>O+ contents in the hydrous minerals

	Igneous minerals					Alteration minerals				
	Apatite	Biotite	Hornblende	Sphene	Epidote	Chlorite	Sphene	Epidote	Hydrogarnet?	Hydrothermal biotite
<b>Laramide rocks:</b>										
Cl	0.02-1.4	0.02-0.26	0.02-0.17	<0.02-0.02	<0.02	<0.02-0.04	-----	<0.02	<0.02	0.06
F	1.2-3.6	.10-0.86	.11-0.58	.08-.30	<.04	<.04-.30	0.18-2.5	<.04-0.11	.60-1.8	1.7
*H <sub>2</sub> O+	.06-1.09	3.52-3.94	1.76-2.00	†.99-1.12	1.86-1.88	.04-.30	-----	-----	-----	3.22
<b>Ruin Granite:</b>										
Cl	.11	.10-0.13	-----	-----	-----	<.02	-----	-----	-----	-----
F	3.3	1.7-1.8	-----	-----	-----	.37-.44	-----	-----	-----	-----
*H <sub>2</sub> O+	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
<b>Precambrian diabase:</b>										
Cl	.83	.24	-----	-----	-----	-----	-----	-----	-----	0.05-0.09
F	2.1	<.04	-----	-----	-----	-----	-----	-----	-----	1.4
*H <sub>2</sub> O+	-----	-----	-----	-----	-----	-----	-----	-----	-----	3.42-3.43

\* Calculated by difference assuming ideal [Cl, F, OH].  
 † Calculated assuming all O<sub>2</sub> oxygen sites occupied by Cl, F, and OH.

) found approxi-  
 0.09 wt percent)

TABLE 3.—Cl, F, and H<sub>2</sub>O+ contents in igneous apatite from Laramide intrusive rocks near the Ray porphyry copper deposit, Arizona

Rock type	Probe sample	Grain		Contents (weight percent)		
		No.	Occurrence <sup>1</sup>	<sup>2</sup> Cl	<sup>2</sup> F	<sup>2</sup> H <sub>2</sub> O+
Tortilla Quartz Diorite.	217-28	1A	H	0.67±0.04	2.4±0.1	0.47
		5A	P	.61±.04	1.6±.1	.88
		5AA	P	.64±.07	2.0±.1	.68
	217-1	1A	P	.97±.07	1.7±.1	.73
		5A	P	1.0±.09	1.9±.1	.63
		7A	M	.67±.05	2.1±.1	.67
	248-29	1A	P	.53±.03	1.6±.1	.87
		2A	P	.42±.01	1.5±.1	.94
		3A	P	.46±.04	1.2±.2	1.09
	Rattler Granodiorite.	46-99B	T17A	H	.80±.02	1.9±.01
T16A			PL	.64±.02	2.4±.1	.53
T19A			M	1.3±.002	1.9±.04	.51
T20A			P	1.4±.02	1.5±.05	.72
60-113D		T22A	P	.73±.02	2.3±.1	.52
		T21A	P	.73±.02	2.2±.1	.54
60-108		1A	P	.14±.01	2.7±.1	.48
		3A	P	.29±.04	2.6±.1	.47
		6A	P	.25±.02	2.5±.1	.53
61-25		T14A	P	.42±.02	2.8±.1	.37
	T15A	GM	.35±.02	2.8±.1	.39	
60-91	1A	P	.34±.02	2.2±.2	.65	
	2A	B	.36±.01	2.3±.2	.60	
	6A	P	.47±.05	2.2±.1	.59	
60-111	2A	P	.75±.05	2.1±.1	.60	
	1A	M	.47±.05	2.3±.2	.57	
60-98	3A	B	.45±.02	2.5±.1	.47	
	6A	P	.47±.01	2.6±.1	.43	
	6A	P	.25±.03	2.5±.2	.50	
246-11G	6AA	P	.23±.02	2.6±.2	.48	
	7A	B	.45±.01	2.5±.2	.46	
	60-131	M1A	P	.62±.02	2.4±.1	.46
60-130	M2A	GM	.58±.03	2.5±.2	.42	
	3A	B	.34±.04	2.7±.1	.40	
260-96A	2A	B	.52±.07	2.2±.2	.59	
	3A	B	.54±.01	2.1±.1	.61	
	3AA	B	.60±.03	2.1±.1	.62	
46-11A	1A	P	.25±.01	2.3±.2	.63	
	3A	B	.20±.02	2.6±.2	.50	
	4A	P	.30±.02	2.8±.1	.37	
	T16-630	3A	P	.34±.04	2.2±.2	.65
Rhyodacite dike.	17-16	7A	B	.57±.02	2.3±.1	.55
		1A	P	.28±.13	2.4±.2	.58
		M1A	P	.37±.17	2.4±.4	.54
Rhyodacite dike.	GM100	M2A	P	.14±.06	2.8±.1	.41
		7A	B	.11±.02	2.3±.3	.67
		XA	P	.09±.02	2.4±.2	.63
Granite Mountain Porphyry.	RB5	YA	P	.08±.04	1.2±.2	1.21
		2A	B	ND	3.0±.1	.36
		3A	B	ND	3.0±.1	.36
	GM14	3AA	B	ND	3.2±.1	.26
		T33A	B	ND	3.0±.1	.39
	GM12	T33B	B	ND	3.1±.1	.32
		2A	B	ND	2.8±.2	.45
		3A	B	ND	3.3±.2	.21
	GM18	4A	B	ND	3.3±.2	.21
		2A	P	ND	3.2±.2	.28
7A		P	ND	3.0±.3	.36	
2GM6G	8A	P	ND	2.9±.1	.42	
	1MA	P	.03±.01	3.2±.1	.24	
	2MA	B	ND	3.6±.2	.06	
2GM1A	5A	P	ND	3.3±.2	.22	
	1A	P	ND	3.5±.3	.13	
	1AA	P	ND	3.0±.5	.29	
2GM2A	2A	P	ND	3.0±.1	.36	
	5A	PL	ND	2.9±.1	.41	
	5AA	PL	.02±.01	3.4±.1	.15	

TABLE 3.—Cl, F, and H<sub>2</sub>O+ contents in igneous apatite from Laramide intrusive rocks near the Ray porphyry copper deposit, Arizona—Continued

Rock type	Probe sample	Grain		Contents (weight percent)		
		No.	Occurrence <sup>1</sup>	<sup>2</sup> Cl	<sup>2</sup> F	<sup>2</sup> H <sub>2</sub> O+
Teapot Moun- tain Por- phyry.	2TTM	1A	B	.13±.02	2.6±.2	.51
		2A	GM	.09±.02	3.3±.1	.20
		5A	B	.12±.01	2.6±.2	.53
		5AA	GM	.11±.01	2.8±.1	.42
Rhyodacite dike.	61-2F	T18A	GM	.77±.03	1.4±.1	.91
		T10A	P	.16±.02	1.7±.1	.92

<sup>1</sup> Grain occurrence: P, phenocryst or large grain; H, inclusion in hornblende; B, inclusion in biotite; M, inclusion in magnetite; PL, inclusion in plagioclase; and GM, groundmass.

<sup>2</sup> Microprobe analysis. Precision calculated from standard counting error from mean of 6 to 10 data points. ND, not detected at 0.02 wt percent Cl.

<sup>3</sup> Calculated assuming ideal [Cl, F, OH].

TABLE 4.—Cl, F, and H<sub>2</sub>O+ contents in Laramide igneous and hydrothermal biotite in and near the Ray porphyry copper deposit, Arizona.

Rock type	Probe sample	Grain No.	Contents <sup>1</sup> (weight percent)		
			<sup>2</sup> Cl	<sup>2</sup> F	<sup>2</sup> H <sub>2</sub> O+
Tortilla Quartz Diorite.	217-28	2BIC	0.13±0.01	0.27±0.01	3.87
		2BIE	.14±.01	.26±.01	3.85
		5BIC	.15±.01	.26±.01	3.80
		5BIE	.13±.02	.25±.05	3.81
		1BIC	.15±.02	.14±.03	3.89
	217-1	1BIE	.15±.02	.16±.02	3.94
		5BI	.17±.01	.19±.04	3.89
		4BIC	.12±.02	.23±.02	3.88
		4BIE	.14±.01	.20±.03	3.94
		3BIC	.18±.003	.27±.04	3.80
Rattler Granodiorite.	246-99B	*3BIE	.19±.003	.30±.06	3.78
		3BIC	.23±.01	.34±.05	3.77
	260-113D	3BIE	.26±.03	.41±.04	3.74
		*4BI	.23±.01	.37±.02	3.75
		1BIC	.15±.004	.46±.03	3.71
	261-25	1BIE	.14±.003	.47±.09	3.73
		3BIC	.14±.003	.54±.05	3.62
		CHEM	.12	.42	3.3
	60-01	2BIC	.18±.01	.34±.03	3.83
		2BIE	.12±.01	.29±.02	3.83
4BIC		.12±.01	.32±.03	3.85	
4BIE		.10±.01	.31±.05	3.88	
5BIC		.13±.01	.31±.04	3.81	
5BIE		.12±.01	.36±.05	3.80	
60-111		2B1C	.18±.01	.39±.03	3.82
		2B1E	.19±.01	.41±.04	3.80
		2B1C	.20±.02	.40±.03	3.78
		2B1E	.19±.01	.38±.03	3.82
	1BIC	.17±.01	.37±.05	3.85	
246-11G	3BIC	.12±.01	.49±.03	3.74	
	3BIE	.14±.01	.46±.04	3.75	
	4BIC	.13±.01	.48±.05	3.74	
	4BIE	.11±.01	.50±.06	3.78	
	1BIC	.13±.01	.38±.03	3.79	
60-131	1BIE	.13±.01	.35±.03	3.82	
	2BIC	.12±.01	.40±.03	3.81	
	2BIE	.11±.01	.38±.04	3.82	
	3BI	.14±.01	.43±.02	3.76	
	4BIC	.13±.01	.45±.03	3.82	

TION

neous apatite from  
porphyry copper de-

Contents (weight percent)	<sup>2</sup> F		<sup>3</sup> H <sub>2</sub> O+
	<sup>2</sup> F	<sup>3</sup> H <sub>2</sub> O+	
.02	2.0±.2	.51	
.02	3.3±.1	.20	
.01	2.6±.2	.53	
.01	2.8±.1	.42	
.03	1.4±.1	.91	
.02	1.7±.1	.92	

Grain: H, inclusion in  
ion in magnetite; Pl,  
on standard counting  
of detected at 0.02 wt

Granite igneous and  
ray porphyry copper

Contents <sup>1</sup> (weight percent)	<sup>2</sup> F		<sup>3</sup> H <sub>2</sub> O+
	<sup>2</sup> F	<sup>3</sup> H <sub>2</sub> O+	
.01	0.27±0.01	3.87	
.01	.26±.01	3.85	
.01	.26±.03	3.80	
.02	.25±.05	3.81	
.02	.14±.03	3.89	
.02	.16±.02	3.94	
.01	.19±.04	3.89	
.02	.23±.02	3.88	
.01	.20±.03	3.94	
.003	.27±.04	3.80	
.003	.30±.06	3.78	
.01	.34±.05	3.77	
.03	.41±.04	3.74	
.01	.37±.02	3.75	
.004	.46±.03	3.71	
.003	.47±.09	3.73	
.003	.54±.05	3.62	
	.42	3.3	
.01	.34±.03	3.83	
.01	.29±.02	3.83	
.01	.32±.03	3.85	
.01	.31±.05	3.88	
.01	.31±.04	3.81	
.01	.36±.05	3.80	
.01	.39±.03	3.82	
.01	.41±.04	3.80	
.02	.40±.03	3.78	
.01	.36±.03	3.82	
.01	.37±.05	3.85	
.01	.49±.03	3.74	
.01	.46±.04	3.75	
.01	.48±.05	3.74	
.01	.50±.06	3.78	
.01	.38±.03	3.79	
.01	.35±.03	3.82	
.01	.40±.03	3.81	
.01	.38±.04	3.82	
.01	.43±.02	3.76	
.01	.45±.03	3.82	

TABLE 4.—Cl, F, and H<sub>2</sub>O+ contents in Larumide igneous and hydrothermal biotite in and near the Ray porphyry copper deposit, Arizona—Continued

Rock type	Probe sample	Grain No.	Contents <sup>1</sup> (weight percent)			
			<sup>2</sup> Cl	<sup>2</sup> F	<sup>3</sup> H <sub>2</sub> O+	
Rattler Granodiorite—Con.	60-130	4BIE	.14±.01	.42±.05	3.80	
		5BI	.18±.01	.43±.03	3.73	
		2BI	.16±.01	.40±.03	3.79	
		3BIC	.15±.01	.45±.04	3.80	
		3BIE	.16±.01	.46±.03	3.78	
		1BIC	.14±.01	.60±.03	3.68	
	246-11A	1BIE	.14±.01	.61±.05	3.66	
		5BIC	.16±.01	.62±.04	3.63	
		5BIE	.15±.01	.62±.05	3.63	
		T16-630	1BI	.10±.01	.31±.03	(*)
			3BI	.11±.001	.28±.03	(*)
			4BI	.11±.01	.34±.04	(*)
5BI	.10±.01		.29±.03	(*)		
9BI	.12±.01	.36±.05	(*)			
Rhyodacite dike.	2GM100	1BIC	.15±.004	.16±.03	3.81	
		1BIE	.09±.01	.25±.01	3.79	
		3BIC	.07±.003	.20±.04	3.85	
		3BIM	.09±.02	.23±.04	3.83	
		3BIE	.06±.01	.25±.07	3.83	
	RB5	6BIC	.04±.02	.56±.03	3.67	
		6BIE	.05±.01	.50±.02	3.69	
		6BIEE	.04±.002	.52±.03	3.68	
		7BIC	.04±.01	.58±.06	3.65	
		7BIE	.03±.01	.59±.03	3.67	
Granite Mountain Porphyry.	2GM14	2BI	.02±.01	.67±.07	3.61	
		2BIA	.02±.01	.61±.04	3.67	
		6BI	.02±.01	.63±.04	3.59	
		GM12	4BI	.05±.01	.61±.07	3.64
			2BI	.03±.01	.69±.05	3.61
			3BI	.05±.01	.61±.05	3.63
	GM18	3BIA	.02±.01	.63±.03	3.65	
		MBIC	.04±.01	.75±.05	3.59	
		MBIE	.04±.003	.72±.05	3.61	
		M1BIC	.03±.01	.82±.05	3.57	
		M1BIE	.02±.004	.81±.04	3.62	
		M2BIC	.03±.01	.62±.06	3.66	
GM6G	M2BIE	.04±.01	.54±.12	3.70		
	3BIA	.02±.006	.66±.06	3.58		
	4BIA	.03±.006	.69±.04	3.60		
	2GM6G	4BI	.03±.01	.76±.13	3.52	
		1BIA	.02±.004	.77±.06	3.59	
	2GM4V	3BIA	.03±.006	.86±.04	3.58	
GM2A	3BIB	.04±.01	.82±.05	3.55		
	1BI	.02±.01	.72±.18	3.60		
Mineralized diabase.	P70-22	1BI	.05±.02	1.4±.1	3.43	
		1BIA	.09±.03	1.4±.2	3.42	
Mineralized Granite Mountain Porphyry.	T123	BI1	.06±.005	1.7±.1	3.22	
		BI2	.06±.003	1.7±.1	3.22	

\* Inclusion in hornblende.  
<sup>1</sup> Precision calculated from standard counting error from the mean of 5 to 10 data points collected within a 10×10 μm area.  
<sup>2</sup> Microprobe analysis.  
<sup>3</sup> Calculated assuming ideal [Cl, F, OH].  
<sup>4</sup> Cl by chemical analysis; J. Budinsky, analyst.  
<sup>5</sup> F and H<sub>2</sub>O+ by chemical analysis; M. Crooner, analyst.  
<sup>6</sup> Incomplete analysis; H<sub>2</sub>O+ was not calculated.

TABLE 5.—Cl, F, and H<sub>2</sub>O+ contents in hornblende from Larumide intrusive rocks near the Ray porphyry copper deposit, Arizona

Rock type	Probe sample	Grain No.	Contents <sup>1</sup> (weight percent)		
			<sup>2</sup> Cl	<sup>2</sup> F	<sup>3</sup> H <sub>2</sub> O+
Tortilla Quartz Diorite.	217-28	2H	0.08±0.007	0.16±0.03	1.92
		3H	.07±.007	.16±.02	1.94
		4H	.09±.012	.13±.04	1.94
	248-29	4HA	.07±.007	.11±.06	1.95
		1H	.02±.004	.12±.03	1.96
		2HC	.03±.009	.14±.03	1.99
Rattler Granodiorite.	246-99B	2HE	.02±.005	.14±.02	2.00
		3H	.03±.004	.15±.03	1.97
		1HC	.10±.007	.19±.05	1.93
	60-113D	1HE	.07±.005	.17±.02	1.93
		2H	.08±.006	.16±.03	1.94
		3HC	.08±.006	.22±.02	1.91
	60-108	3HM	.08±.006	.22±.02	1.91
		3HE	.09±.012	.14±.02	1.98
		M1HC	.09±.010	.24±.02	1.89
		MHE	.13±.008	.24±.02	1.90
		M1HE	.17±.013	.21±.01	1.87
		M1HE	.14±.007	.22±.03	1.88
261-25	M2HC	.17±.006	.23±.02	1.85	
	M2HE	.12±.010	.23±.03	1.88	
	1H	.09±.009	.48±.06	1.76	
	4HC	.05±.007	.58±.03	1.77	
	4HE	.09±.005	.48±.02	1.79	
	6HC	.06±.004	.45±.05	1.83	
T16-630	6HE	.09±.005	.54±.04	1.79	
	4H	.05±.008	.14±.05	(*)	
	6H	.03±.007	.14±.03	(*)	
	8H	.04±.007	.21±.03	(*)	
	60-91	MH	.08±.010	.30±.03	1.84
		4H	.04±.013	.27±.02	1.93
5HC		.07±.002	.26±.01	1.80	
246-11G	5HE	.06±.002	.31±.01	1.83	
	MH	.10±.013	.21±.02	1.85	
	4MHC	.05±.004	.22±.04	1.93	
	4MHE	.05±.002	.18±.01	1.91	
	1MH	.03±.06	.22±.02	1.95	
	60-98	MHC	.04±.008	.24±.03	1.86
Rhyodacite dike.	17-16	MHE	.04±.021	.24±.02	1.90
		1MH	.05±.010	.27±.04	1.86
		3H	.04±.016	.30±.04	1.89
	GM100	5HC	.06±.017	.28±.03	1.91
		5HE	.06±.038	.26±.04	1.93
		7HC	.04±.010	.29±.02	1.91
Rhyodacite dike.	GM18	7HE	.04±.001	.26±.02	1.93
		MHC	.14±.012	.17±.03	1.87
		MHE	.15±.009	.17±.02	1.87
	GM100	M1H	.15±.015	.15±.04	1.89
		2HC	.13±.010	.17±.05	1.88
		2HE	.15±.011	.17±.03	1.89
Granite Mountain Porphyry.	GM18	MH	.03±.005	.12±.03	1.98
		M1H	.08±.024	.14±.02	1.90
		M2H	.04±.010	.13±.03	1.97
Granite Mountain Porphyry.	GM18	T1HC	.06±.007	.38±.03	1.79
		T1HE	.08±.005	.39±.04	1.77

<sup>1</sup> Precision for Cl and F calculated from standard counting error from the mean of 5 to 10 data points collected within a 10×10 μm area.  
<sup>2</sup> Microprobe analysis.  
<sup>3</sup> Calculated assuming ideal [Cl, F, OH].  
<sup>4</sup> Incomplete analysis; H<sub>2</sub>O+ was not calculated.

TABLE 6.—Cl, F, and H<sub>2</sub>O+ contents in igneous (?) epidote and igneous sphene from Laramide intrusive rocks near the Ray porphyry copper deposit, Arizona

Rock type	Probe sample	Grain No.	Contents (weight percent)		
			<sup>35</sup> Cl	<sup>19</sup> F	<sup>2</sup> H <sub>2</sub> O+
Epidote analyses					
Tortilla Quartz Diorite.	217-1	6PE <sup>3</sup>	ND	ND	1.88
Rattler Granodiorite.	246-99B	MPE <sup>3</sup>	ND	ND	1.86
Sphene analyses					
Tortilla Quartz Diorite.	217-1	6PS <sup>3</sup>	0.02±0.007	0.09±0.02	1.10
	217-28	2PS <sup>4</sup>	ND	.09±.04	1.12
Rattler Granodiorite.	246-99B	4PS <sup>4</sup>	ND	.08±.02	1.12
	246-11G	MPSC <sup>4</sup>	ND	.12±.02	1.07
		MPSE <sup>4</sup>	ND	.12±.03	1.07
		7PS <sup>5</sup>	ND	.16±.03	1.06
	261-25	MPS <sup>4</sup>	ND	.12±.02	1.08
	T16-630	2PS <sup>4</sup>	ND	.08±.02	(*)
		10PS <sup>4</sup>	ND	.09±.01	(*)
Granite Mountain Porphyry.	RB5	5PSC <sup>4</sup>	ND	.25±.03	1.03
		5PSE <sup>4</sup>	ND	.24±.02	1.02
	2GM14	4PS <sup>5</sup>	ND	.30±.03	.99

<sup>1</sup> Microprobe analysis. Precision calculated from standard counting error from the mean of 5 to 10 data points within a 10×10 μm area. ND, not detected at 0.02 wt percent Cl, 0.04 wt percent F.

<sup>2</sup> Calculated assuming ideal (Cl, F, OH).

<sup>3</sup> Interstitial to feldspar and Fe-Mg silicates.

<sup>4</sup> Phenocryst or large grain.

<sup>5</sup> Included in biotite.

\* Incomplete analysis; H<sub>2</sub>O+ not calculated.

TABLE 7.—Cl and F contents in chlorite derived from biotite in Laramide igneous rocks in and near the Ray porphyry copper deposit, Arizona

Rock type	Probe sample	Grain No.	Contents <sup>1</sup> (weight percent)	
			<sup>35</sup> Cl	<sup>19</sup> F
Tortilla Quartz Diorite.	217-28	5CL	ND	ND
Rattler Granodiorite.	246-99B	1CLA	ND	ND
		1CLB	0.03±0.012	0.10±0.02
		2CLA	ND	ND
		2CLB	ND	ND
	260-113D	3CLA	.04±.001	.05±.001
		3CLB	.03±.004	.08±.02
		4CLA	.03±.003	.13±.03
		4CLB	ND	.08±.03
	261-25	2CLA	ND	.07±.02
		2CLB	ND	.16±.07
	246-11G	2CLA	ND	.09±.03
		2CLB	ND	.11±.01
		4CL	ND	.11±.001
	260-96A	3CL	ND	.12±.001
	246-11A	1CLA	.03±.007	.30±.04
		1CLB	.03±.008	.24±.03
		5CLA	.02±.008	.15±.03
		5CLB	.02±.006	.27±.02
	T16-630	1CL	ND	.12±.03
		5CL	ND	.09±.01
		8CL	ND	.13±.05
		10CL	ND	.10±.04
	2GM14	2CL	ND	.12±.03
		6CL	ND	.13±.03
		6CLA	ND	.10±.03
Granite Mountain Porphyry.	GM12	3CL	ND	.14±.02
		3CLA	ND	.13±.02
		4CL	ND	.14±.04

TABLE 7.—Cl and F contents in chlorite derived from biotite in Laramide igneous rocks in and near the Ray porphyry copper deposit, Arizona—Continued

Rock type	Probe sample	Grain No.	Contents <sup>1</sup> (weight percent)	
			<sup>35</sup> Cl	<sup>19</sup> F
Granite Mountain Porphyry—Continued	GM6G	3CLA	ND	.09±.03
		4CLA	ND	.16±.03
	2GM6G	4CL	ND	.06±.04
		6CL	ND	.07±.06
		6CLA	ND	.10±.06
	2GM4V	1CL	ND	.16±.03
		1CLA	ND	.19±.04
		3CL	ND	.23±.04
	2GM2A	3CL	ND	.18±.09
		4CL	ND	.16±.05
		5CL	ND	.16±.11
	2GM1A	2CL	.03±.009	.23±.08
		2CLA	.03±.013	.27±.13
		2CLB	.03±.008	.26±.13
Mineralized diabase.	P70-22	1CL	.05±.016	.27±.13

<sup>1</sup> Precision calculated from standard counting error from the mean of 4 to 10 data points within a 10×10 μm area.

<sup>2</sup> Microprobe analysis. ND, not detected at 0.02 wt percent Cl, 0.04 wt percent F.

TABLE 8.—Cl and F contents in minerals formed from biotite, plagioclase, pyroxene, and chlorite in Laramide intrusive rocks near the Ray porphyry copper deposit, Arizona

Rock type	Probe sample	Grain No.	Contents <sup>1</sup> (weight percent)	
			<sup>35</sup> Cl	<sup>19</sup> F
Epidote after biotite				
Tortilla Quartz Diorite.	217-1	6SE	ND	ND
Rattler Granodiorite.	260-113D	2SE	ND	0.11±0.05
		5SE	ND	.07±.02
	261-25	1SE	ND	.09±.08
	246-11G	2SE	ND	.05±.02
Granite Mountain Porphyry.	RB5	4SE	ND	.06±.01
	2GM6G	1SE	ND	.04±.03
Sphene after biotite				
Tortilla Quartz Diorite.	217-1	3SS	ND	0.51±0.05
Rattler Granodiorite.	246-99B	1SS	ND	1.4 ± .2
	261-25	1SS	ND	.18±.01
	246-11G	2SS	ND	2.2 ± .1
		3SS	ND	1.3 ± .2
		6SS	ND	1.0 ± .03
	246-11A	4SS	ND	1.1 ± .1
	T16-630	1SS	ND	.74±.15
		8SS	ND	1.2 ± .07
		10SS	ND	.66±.05
Granite Mountain Porphyry.	RB5	4SS	ND	1.7 ± .2
		5SS	ND	1.5 ± .2
	GM12R	4SS	ND	.20±.02
		3SS	ND	.50±.03
	2GM14	6SSA	ND	.66±.09
		6SSB	ND	.49±.10
	GM6G	2D	0.09±0.02	2.5 ± .3
	2GM6G	6SSA	ND	.44±.04
		6SSB	ND	.65±.03

derived from biotite in the Ray porphyry copper

Contents <sup>1</sup> (weight percent)	
<sup>37</sup> Cl	<sup>19</sup> F
ND	.09 ± .03
ND	.16 ± .03
ND	.06 ± .04
ND	.07 ± .06
ND	.10 ± .06
ND	.16 ± .03
ND	.19 ± .04
ND	.23 ± .04
ND	.18 ± .09
ND	.16 ± .05
ND	.16 ± .11
.03 ± .009	.23 ± .08
.03 ± .013	.27 ± .13
.03 ± .008	.26 ± .13
.05 ± .016	.27 ± .13

Counting error from the mean for 0.02 wt percent Cl, 0.04

minerals formed from biotite in Laramide intrusive rocks near the Ray porphyry copper deposit, Arizona

Contents <sup>1</sup> (weight percent)	
<sup>37</sup> Cl	<sup>19</sup> F
ND	ND
ND	ND
ND	.11 ± 0.05
ND	.07 ± .02
ND	.09 ± .08
ND	.05 ± .02
ND	.06 ± .01
ND	.04 ± .03

Contents <sup>1</sup> (weight percent)	
<sup>37</sup> Cl	<sup>19</sup> F
ND	.51 ± 0.05

ND	1.4 ± .2
ND	.18 ± .01
ND	2.2 ± .1
ND	1.3 ± .2
ND	1.0 ± .03
ND	1.1 ± .1
ND	.74 ± .15
ND	1.2 ± .07
ND	.66 ± .05
ND	1.7 ± .2
ND	1.5 ± .2
ND	.20 ± .02
ND	.50 ± .03
ND	.66 ± .03
ND	.49 ± .10
0.09 ± 0.02	2.5 ± .3
ND	.44 ± .04
ND	.65 ± .03

TABLE 8.—Cl and F contents in minerals formed from biotite, plagioclase, pyroxene, and chlorite in Laramide intrusive rocks near the Ray porphyry copper deposit, Arizona—Continued

Rock type	Probe sample	Grain No.	Contents <sup>1</sup> (weight percent)	
			<sup>37</sup> Cl	<sup>19</sup> F
Phengite and clay analyses				
Tortilla Quartz Diorite.	217-1	MSP <sup>2</sup>	0.03 ± 0.03	ND
Granite	2GM14	4SPA <sup>3</sup>	ND	ND
Mountain	GM12R	4SPA <sup>3</sup>	ND	0.04 ± 0.05
Porphyry	GM2A	4P <sup>4</sup>	ND	.55 ± .02
		5P <sup>4</sup>	ND	.45 ± .08
Hydrogarnet(?) after biotite				
Tortilla Quartz Diorite.	217-28	4M	ND	0.69 ± 0.10
Rattler Granodiorite.	260-113D T16-630	3M	ND	1.8 ± .1
		5M	ND	1.4 ± .1
		9M	ND	1.6 ± .1
Fibrous amphibole analysis				
Tortilla Quartz Diorite.	217-1	MFHB <sup>5</sup>	0.02 ± 0.008	0.11 ± 0.03

<sup>1</sup>Precision calculated from standard counting error from the mean of 5 to 10 data points within a 10 × 10 μm area.  
<sup>2</sup>Microprobe analysis. ND, not detected at 0.02 wt percent Cl, 0.04 wt percent F.  
<sup>3</sup>Alteration product of plagioclase.  
<sup>4</sup>Alteration product of chlorite.  
<sup>5</sup>Reaction rim on pyroxene.

TABLE 9.—Cl and F contents in igneous and alteration minerals from Precambrian intrusive rocks near the Ray porphyry copper deposit, Arizona

Rock type (Sample No.)	Mineral	Grain No.	Contents <sup>1</sup> (weight percent)	
			<sup>37</sup> Cl	<sup>19</sup> F
Ruin Granite (PCR).	Biotite	2BI	0.13 ± 0.01	1.7 ± 0.07
		3BI	.12 ± .01	1.7 ± .09
		3B12	.11 ± .004	1.7 ± .04
		M1BI	.10 ± .01	1.8 ± .15
		2CL	ND	.44 ± .01
Diabase (DBA-32).	Biotite	3CL	ND	.43 ± .03
		4CL	ND	.37 ± .04
		3A	.11 ± .02	3.3 ± .14
		3A2	.11 ± .01	3.3 ± .09
Apatite	MBI	.24 ± .04	ND	
	7A	.83 ± .03	2.1 ± .28	

<sup>1</sup>Precision calculated from standard counting error from the mean of 5 to 8 data points in a 10 × 10 μm area.  
<sup>2</sup>Microprobe analysis. ND, not detected at 0.02 wt percent Cl, 0.04 wt percent F.

fine to resolve, and also one grain of fibrous amphibole formed from pyroxene are included in table 8. Cl occurs near or below detection level in the clay, phengites, and amphibole; only the intensely altered area in the plagioclase, the phengite derived from chlorite, and the amphibole contain detectable amounts of F.

Intrasample variations and zoning

The igneous minerals in the Laramide rocks studied have not been homogenized with respect to the halogens (or other constituents; author, unpub. data) by exchange with magma, magmatic fluid, or postmagmatic fluid. Measurably different abundances of one or both halogens occur between like-mineral grains in the same sample (40 percent of the samples for apatite, 25 percent for biotite, and 35 percent for hornblende) and zoning of major and (or) minor elements is found in apatite, biotite, and hornblende as well as in plagioclase. Analytically distinguishable zoning of Cl or F, or both, occurred in 11 of 34 apatite grains and in 9 of 16 hornblende grains studied for zoning, whereas zoning of the halogens in biotite was seldom detected (compare grain numbers ending in C, centers, and E, edges; table 4). Neither the zoning or abundance of Cl or F in the igneous minerals seems related to the amount of plagioclase or mafic minerals altered in a sample (table 1), proximity of altered grains to the one analyzed, or the potential susceptibility of a grain to exchange by virtue of its size or inclusion in other minerals. (See mineral occurrence data in table 3, and in footnotes of tables 4 and 6.) However, although the minerals have not been homogenized with respect to the halogens, there are no firm trends in the variations (figs. 6 and 7). This suggests that if the observed abundances and variations retain an imprint of those obtained from the magma, then the conditions controlling uptake of Cl, F, and H<sub>2</sub>O by the minerals from the magma were complex. Not enough data were collected for epidote or sphene to make conclusions regarding zoning of Cl and F.

Intersample variations with rock chemistry, Laramide rocks

The abundances of Cl, F, and H<sub>2</sub>O+ in the igneous minerals vary measurably between samples, and these variations appear to be related to greater or lesser degree to variations in whole-rock chemistry (as indicated by differentiation indices, D.I., of the samples). The abundance of Cl in apatite and biotite correlates negatively with rock D.I. (fig. 8), the abundance of F in apatite, biotite, sphene, and perhaps hornblende correlates positively with rock D.I. (fig. 9; tables 6 and 1 for sphene), and the abundance of calculated H<sub>2</sub>O+ in apatite, biotite, sphene, and perhaps hornblende correlates negatively with rock D.I. (fig. 10; tables 6 and 1 for sphene). Correlations of the mineral contents of Cl, F, and H<sub>2</sub>O+ with rock D.I. for the samples from the Rattler Granodiorite generally mirror but are not as strong as those for the entire sample suite. Table 10



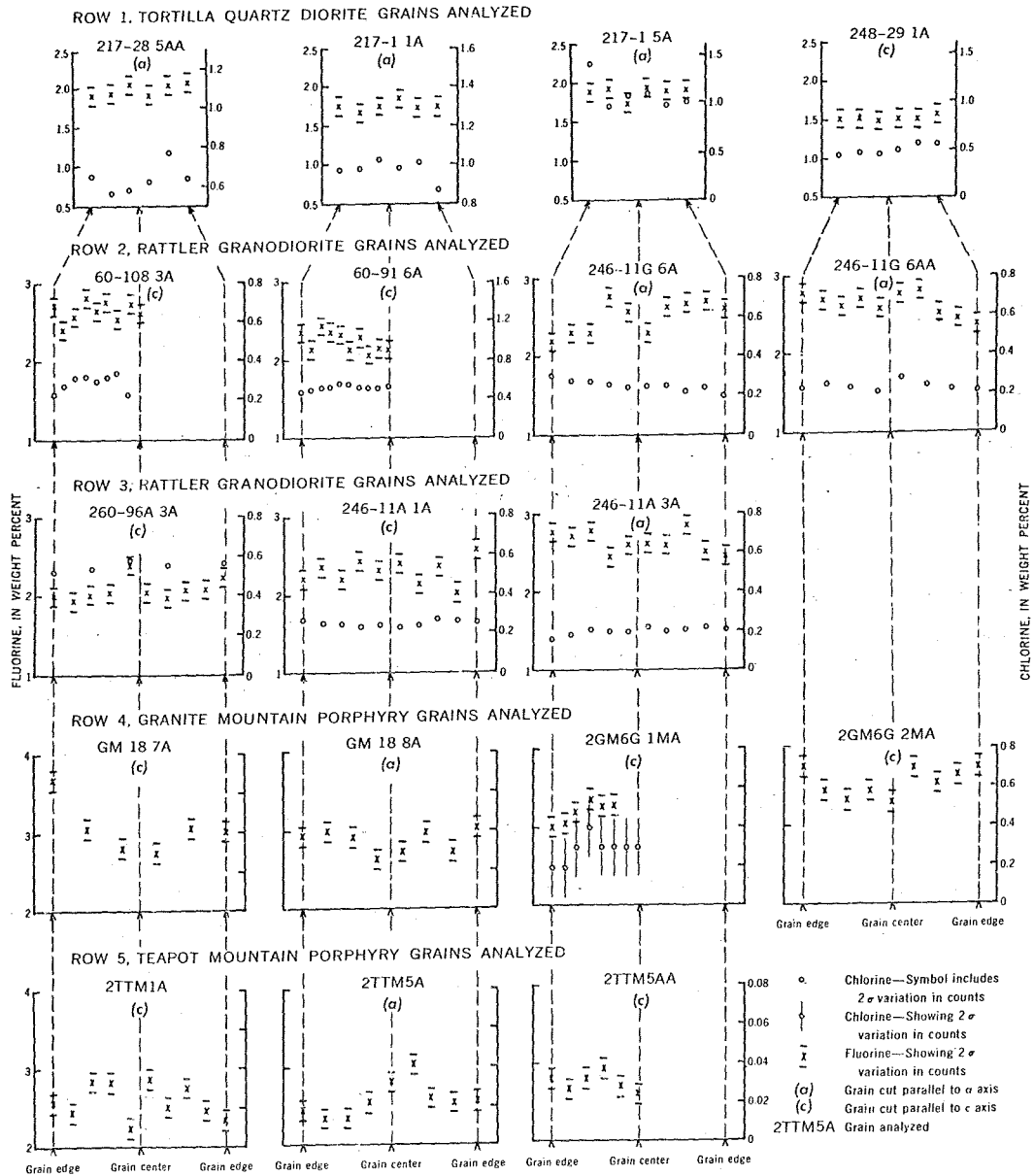


FIGURE 7.—Distribution of Cl and F in individual apatite grains in Tortilla Quartz Diorite, Rattler Granodiorite, Granite Mountain Porphyry, and Teapot Mountain Porphyry.

presents statistical data for figures 8-10. The Pearson correlation assumes that the samples are representative of a larger population, whereas the Spearman rank correlation simply ranks the sample data without any weighting of the samples. Thirty percent of the trends considered have correlation coefficients exceed-

ON

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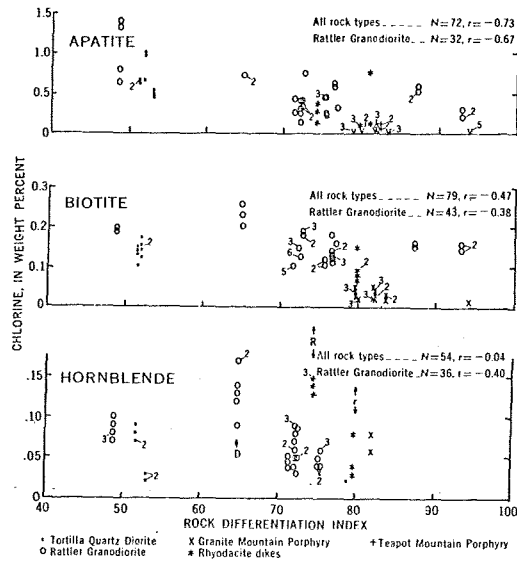


FIGURE 8.—Variations of Cl content of mineral with rock differentiation index.

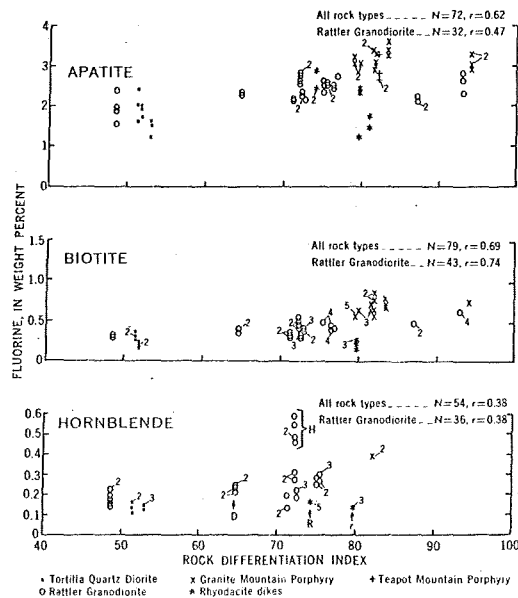


FIGURE 9.—Variations of F content of mineral with rock differentiation index.

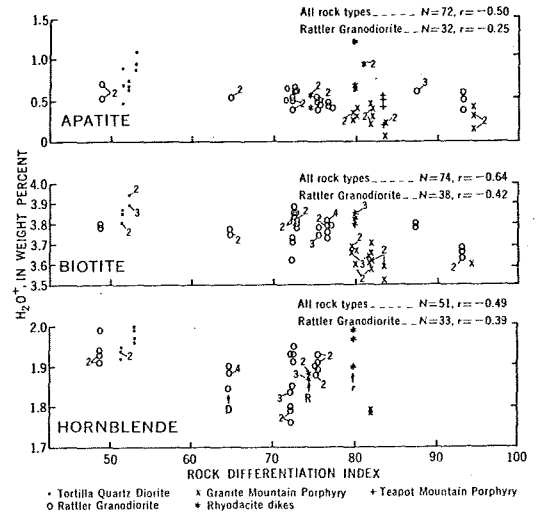


FIGURE 10.—Variations of calculated H<sub>2</sub>O<sup>+</sup> content of mineral with rock differentiation index.

ing [0.65] and are thought to have geological significance. Fifty-five percent of the trends have correlation coefficients that exceed |0.50|, and all but one of those with coefficients less than |0.65| have the same slope as the trends with high correlation coefficients.

The positive association of the abundance of F and a negative or lack of association of the abundance of Cl and H<sub>2</sub>O<sup>+</sup> in the minerals with increasing differentiation index of the host rock is not unique to the Ray igneous suite. Goldschmidt (1954) found that the F content of igneous minerals increases as the host rock becomes more felsic. The Cl and H<sub>2</sub>O<sup>+</sup> contents are higher and the F contents lower in apatites from mafic rocks than in apatite from more felsic rocks (A. Kind, cited by Correns, 1956; Taborszky, 1962). Nash (1972a, b) reported that the F content of apatite increased with differentiation of the Iron Hill complex and Shonkin Sag laccolith, and his data indicate that the Cl content of apatite either remained the same or decreased as the host rocks became more differentiated in both intrusive suites. Lee and Van Loenen (1970) found that the F content of biotite increases with decreasing CaO content of hybrid rocks of the southern Snake Range, Nev., and the data of Ivanov (1971). Dodge and Moore (1968), Dodge and others (1968, 1969), Dodge and Ross (1971) suggest the same for F content of biotite from igneous rocks of central Chukotka, Russia, the Sierra Nevada batholith, and the

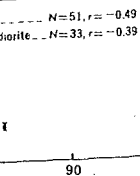
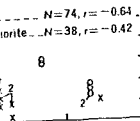
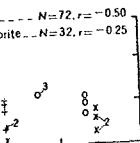


TABLE 10.—Statistical data for Cl, F, and H<sub>2</sub>O+ contents of minerals and rocks plotted against differentiation index (figures 8–12)

Rock type	Mineral	Cl, F, and H <sub>2</sub> O+ in mineral	Pearson correlation			Spearman rank correlation				
			r	N	Confidence level	Coefficient	t test	Degrees of freedom	Confidence level	
Data from figure 8										
All	Apatite	Cl	-0.73	72	>.99	-0.69	-8.0	70	>.99	
	Biotite	Cl	-.47	79	>.99	-.51	-5.2	77	>.99	
	Hornblende	Cl	-.04	54	---	-.18	-1.35	52	>.85	
	Rattler Granodiorite	Apatite	Cl	-.67	32	>.99	-.40	-2.45	30	>.95
		Biotite	Cl	-.23	43	<.95	.01	.05	41	---
		Hornblende	Cl	-.10	46	>.95	-.60	-4.43	34	>.99
Data from figure 9*										
All	Apatite	F	0.62	72	>.99	0.59	6.2	70	>.99	
	Biotite	F	.09	79	>.99	.74	9.7	77	>.99	
	Hornblende	F	.54	54	>.99	.34	2.57	52	>.85	
	Rattler Granodiorite	Sphene	F	.66	12	>.95	.94	8.2	10	>.99
		Apatite	F	.47	32	>.99	.29	1.64	30	>.90
		Biotite	F	.74	43	>.99	.65	5.5	41	>.99
Rattler Granodiorite	Hornblende	F	.38	36	>.95	.48	3.23	34	>.99	
	Sphene	F	.58	7	<.95	.89	( <sup>b</sup> )	( <sup>b</sup> )	( <sup>b</sup> )	
Data from figure 10*										
All	Apatite	H <sub>2</sub> O+	-0.50	72	>.99	-0.52	-5.1	70	>.99	
	Biotite	H <sub>2</sub> O+	-.04	74	>.99	-.66	-7.6	72	>.99	
	Hornblende	H <sub>2</sub> O+	-.49	51	>.99	-.31	-2.25	49	>.99	
	Rattler Granodiorite	Sphene	H <sub>2</sub> O+	-.87	10	>.95	-.98	-1.59	8	>.85
		Apatite	H <sub>2</sub> O+	-.25	32	<.95	-.24	-1.32	30	>.85
		Biotite	H <sub>2</sub> O+	-.42	38	>.99	-.17	-1.01	36	>.80
Rattler Granodiorite	Hornblende	H <sub>2</sub> O+	-.39	33	>.85	-.04	-2.13	31	>.95	
	Sphene	H <sub>2</sub> O+	-.97	5	>.95	-.92	( <sup>b</sup> )	( <sup>b</sup> )	( <sup>b</sup> )	
Data from figure 11										
All	A	Cl	-0.75	20	>.99	-0.81	-5.9	18	>.99	
	Rattler Granodiorite	Cl	-.70	11	>.95	-.55	-1.93	9	>.90	
	A	F	-.39	20	<.95	-.29	-1.30	18	>.80	
	Rattler Granodiorite	F	-.57	11	>.95	-.66	-2.54	9	>.95	
Data from figure 12										
All	A	H <sub>2</sub> O+	-0.36	27	<.95	-0.39	-2.10	25	>.95	
	B	H <sub>2</sub> O+	-.44	22	>.95	-.34	-1.62	20	>.90	
	C	H <sub>2</sub> O+	-.80	20	>.99	-.70	-4.13	18	>.99	
	Rattler Granodiorite	A	H <sub>2</sub> O+	-.16	18	---	-.27	-1.13	16	>.80
		B	H <sub>2</sub> O+	-.40	13	<.95	-.27	-0.2	11	>.99
		C	H <sub>2</sub> O+	-.83	11	>.99	-.61	-2.30	9	>.95

\* Sphene not included in figures 9 and 10. <sup>b</sup> Small sample set.

TION



+ Teapot Mountain Porphyry

content of mineral index.

geological significance have correlation but one of those the same slope as apatites.

abundance of F and a abundance of Cl increasing differentiation technique to the Ray found that the F contents as the host rock H<sub>2</sub>O+ contents are apatites from mafic rocks (A. Kind, 1962). Nash (1972a, apatite increased Hill complex and indicate that the differentiated in Loenen (1970) increases with decrease of the southern of Ivanov (1971), and others (1968, 1969), but the same for F contents of central Chualar batholith, and the

California Transverse and Coast Ranges. In addition, the Cl and H<sub>2</sub>O+ contents of biotite and hornblende in the Sierra Nevada batholith (data of Dodge and others, 1968, 1969), intrusive rocks of the Coast and Transverse Ranges (data of Dodge and Ross, 1971), and of Scandinavian granites (Gillberg, 1964) either correlate negatively or do not correlate with increasing host rock acidity.

#### Intersample variations with sample age, Laramide rocks

Minerals from the oldest Laramide stocks at Ray (Tortilla Quartz Diorite, Rattler Granodiorite) generally contain more Cl and H<sub>2</sub>O+ and less F than

minerals from the younger stocks (Granite Mountain Porphyry, Teapot Mountain Porphyry). This correlation between the age of a pluton and the Cl, F, and H<sub>2</sub>O+ content of its minerals is expected because the contents of these components in the minerals appear related to rock chemistry and, in general, there is a negative correlation between rock differentiation index and the age of the rock type. There are five exceptions: (1) Apatite from the Teapot Mountain Porphyry contains about the same or a little more Cl and H<sub>2</sub>O+ and perhaps less F than apatite in the older Granite Mountain Porphyry; (2) hornblende in sample 17-16 (R in figs. 8-10) contains more Cl than hornblende in

the Tortilla Quartz Diorite which it cuts; (3) biotite in sample GM100 (*r* in figs. 8-10) contains less F and more H<sub>2</sub>O+ than the older Rattler Granodiorite; (4) apatite in sample 61-2F (asterisk symbols in figs. 8-10 plotted at greater than 80 differentiation index), which may be the youngest intrusive type studied, contains less F and more Cl and H<sub>2</sub>O+ than apatite from the Granite Mountain Porphyry; and (5) hornblende and biotite in sample 60-113D (*D* in figs. 8-10), which was intruded as a late dike in the Rattler Granodiorite but prior to aplite development (Cornwall and others, 1971), contain more Cl than do the hornblende and biotite from the samples cut by the dike.

Four of the five exceptions involve minerals from dikes that probably were more susceptible than the stocks to gain and loss of Cl, F, and H<sub>2</sub>O+ by diffusion and contamination. Moreover, for most of the exceptions, only one or two rather than all three components are present in a given mineral in amounts anomalous for the age of the sample, and in several of the exceptions, one of the other coexisting minerals does not show the anomaly.

#### Intersample variations with rock texture and modal abundance, Laramide rocks

Porphyritic texture is sometimes attributed to the buildup and release of volatiles from a cooling magma (pressure quenching, Jahns and Tuttle, 1963). Thus one should perhaps expect the hydrous minerals in porphyritically textured rocks to have different halogen and water contents compared to like minerals in nonporphyritic rocks. However, the halogen and water contents of the igneous minerals are not consistently related to the texture (even porphyritic texture) of the rock. (Compare rock textures in table 1 with data in tables 3-5 or figures 8-10).

Competition for the available water and halogens in the magmas also might be expected to affect the amount of water and halogens incorporated by the minerals, and this might be detected by comparing the compositions of like minerals from samples from the same rock type having like differentiation index but different modal composition. However, a consistent pattern does not emerge from such comparisons. For example, hornblende in sample 48-29 (Tortilla Quartz Diorite) contains three times less Cl and is three times as abundant as the hornblende in sample 17-28, but the F contents of the hornblende in the two samples are not appreciably different. Similarly, samples 61-25 and 60-91 of the Rattler Granodiorite have almost identical differentiation indices as those of samples 60-108 and 60-111 and contain half the amount of biotite (about 6 percent) as that in sample 60-111, which contains no

hornblende, and half the amount of hornblende (about 4 percent) as that of sample 60-108, which contains no biotite. Thus because there are about two times fewer sites for halogens in sample 60-108, one would expect to find more halogens in hornblende of sample 60-108 than in hornblende of samples 61-25 and 60-91; hornblende of sample 60-108 contains comparably more F but not more Cl. Likewise one would perhaps expect a little less of the halogens in the biotite of sample 60-111 compared to that in biotite of samples 61-25 and 60-91. However, biotite in sample 60-111 contains a little more Cl, and about the same amount of F as biotite in samples 61-25 and 60-91.

#### Cl, F, and H<sub>2</sub>O variations with changes in mineral chemistry

The uptake of the halogens and water by the hydrous minerals may be affected by the substitution of other elements in the minerals. This possibility, although considered secondary compared to the variations linked to changes in magma chemistry and age (figs. 8-10), was investigated by comparing variations of halogen abundances with variations in the abundances of other elements in (1) individual grains (zoning) and in (2) all like-mineral grains from the same stock or rock type and from all rock types. For the first comparison, the number and type of correlation (positive, negative, or none) were tabulated for all grains that were studied for zoning in each rock type. No trends emerged from these data for apatite, biotite, and hornblende (summarized in table 11). The data for sphene and epidote were not sufficient for this type of comparison. For the second comparison, correlation matrices were constructed to check for coupled substitution between Cl and F and other elements in the minerals. In these data, trends did emerge for certain elements in apatite, biotite, and hornblende (tables 12-14). However, the correlations do not determine whether Cl, F, and H<sub>2</sub>O+ vary in abundance in response to substitution of the other elements in the minerals (with the possible exception of Cl with Mg and Fe in hornblende) or whether the abundance of the halogens and water as well as the other elements in the minerals all changed in response to changes in the magma(s). For example, the MgO content of biotite correlates positively with the Cl content of biotite, but because Cl and MgO of biotite both vary negatively in abundance with the differentiation index of the samples, it is unclear whether Cl varies in abundance mainly because of coupled substitution with Mg or mainly because of changes in the magma. In view of the zoning studies and the similar correlations between Cl abundance in other minerals and rock chemistry, the changes

in magma are considered most likely. The same is probable for the other correlations between the abundance of an element in biotite, apatite, or hornblende and the abundance of Cl, F, or H<sub>2</sub>O+ in the mineral because they either are not consistent from rock type to rock type, are not significant, or are matched by appropriate negative or positive correlations with rock differentiation index.

TABLE 11.—Comparative zoning of halogens and oxides in apatite, biotite, and hornblende  
[Data are number of correlations tabulated for all grains studied]

	Halogen and oxide							
	Detectably and antipathetically zoned		Detectably and antipathetically zoned		Halogen only or oxide only detectably zoned		Halogen or oxide not detectably zoned	
	Cl	F	Cl	F	Cl	F	Cl	F
<b>Apatite:</b>								
SiO <sub>2</sub>	1	1	1	0	11	15	35	35
CaO	0	0	0	0	4	7	47	44
Na <sub>2</sub> O	0	2	0	1	16	14	35	34
P <sub>2</sub> O <sub>5</sub>	0	0	0	0	4	7	47	44
<b>Biotite:</b>								
SiO <sub>2</sub>	0	0	2	1	5	7	22	21
Al <sub>2</sub> O <sub>3</sub>	1	0	0	0	11	12	17	17
FeO*	1	1	2	1	7	10	19	17
MgO	0	1	3	2	14	12	13	14
MnO	2	0	1	2	5	4	21	23
TiO <sub>2</sub>	2	1	0	2	10	10	17	16
K <sub>2</sub> O	3	2	1	1	4	7	21	19
<b>Hornblende:</b>								
SiO <sub>2</sub>	0	1	3	3	9	4	4	8
Al <sub>2</sub> O <sub>3</sub>	4	3	0	2	9	7	3	4
FeO*	1	2	2	2	9	7	4	5
MgO	0	1	2	0	3	9	6	6
CaO	0	0	1	0	6	7	9	9
TiO <sub>2</sub>	5	3	0	3	7	5	4	5
Na <sub>2</sub> O†	2	0	1	0	3	5	1	5
K <sub>2</sub> O†	2	2	0	3	6	3	1	1

\* All Fe calculated as FeO.

† Fewer correlations for Na<sub>2</sub>O and K<sub>2</sub>O.

TABLE 12.—Partial correlation matrices of apatite chemistry and rock differentiation index  
[Italic figures represent correlation at less than 95-percent confidence level, N, number of observations in a population]

	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	D.I.
<b>Tortilla Quartz Diorite (N, 9)</b>					
Cl	<i>0.38</i>	<i>0.23</i>	<i>0.28</i>	<i>0.22</i>	<i>0.33</i>
F	<i>.21</i>	<i>.32</i>	<i>.15</i>	<i>.13</i>	<i>.26</i>
D.I.	<i>-.13</i>	<i>.44</i>	<i>.97</i>	<i>.72</i>	<i>1.00</i>
<b>Rattler Granodiorite (N, 30)</b>					
Cl	<i>-0.09</i>	<i>-0.37</i>	<i>-0.08</i>	<i>0.37</i>	<i>-0.67</i>
F	<i>.09</i>	<i>.16</i>	<i>.00</i>	<i>.31</i>	<i>.47</i>
D.I.	<i>.25</i>	<i>.06</i>	<i>.52</i>	<i>-.59</i>	<i>1.00</i>
<b>Granite Mountain Porphyry (N, 17)</b>					
Cl	<i>-0.12</i>	<i>-0.20</i>	<i>0.01</i>	<i>-0.35</i>	<i>0.29</i>
F	<i>.03</i>	<i>.50</i>	<i>-.03</i>	<i>-.24</i>	<i>.04</i>
D.I.	<i>.26</i>	<i>-.01</i>	<i>.36</i>	<i>-.34</i>	<i>1.00</i>
<b>All rock types (N, 70)</b>					
Cl	<i>0.08</i>	<i>-0.12</i>	<i>0.12</i>	<i>0.20</i>	<i>-0.73</i>
F	<i>-.03</i>	<i>-.12</i>	<i>-.06</i>	<i>-.20</i>	<i>.62</i>
D.I.	<i>.09</i>	<i>-.13</i>	<i>.29</i>	<i>-.10</i>	<i>1.00</i>

TABLE 13.—Partial correlation matrices of biotite chemistry and rock differentiation index  
[Italic figures represent correlation at less than 95-percent confidence level, N, number of observations in a population]

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO*	MgO	MnO	TiO <sub>2</sub>	K <sub>2</sub> O	D.I.
<b>Tortilla Quartz Diorite (N, 9)</b>								
Cl	<i>-0.08</i>	<i>-0.40</i>	<i>0.05</i>	<i>0.03</i>	<i>-0.35</i>	<i>0.23</i>	<i>0.16</i>	<i>0.41</i>
F	<i>-.32</i>	<i>.55</i>	<i>.37</i>	<i>-.43</i>	<i>.74</i>	<i>-.65</i>	<i>-.47</i>	<i>-.85</i>
D.I.	<i>.55</i>	<i>-.46</i>	<i>-.76</i>	<i>.61</i>	<i>-.91</i>	<i>.88</i>	<i>.65</i>	<i>1.00</i>
<b>Rattler Granodiorite (N, 35)</b>								
Cl	<i>-0.18</i>	<i>-0.08</i>	<i>0.01</i>	<i>0.11</i>	<i>-0.10</i>	<i>-0.26</i>	<i>0.21</i>	<i>-0.28</i>
F	<i>-.26</i>	<i>-.22</i>	<i>-.19</i>	<i>.12</i>	<i>.06</i>	<i>.22</i>	<i>.50</i>	<i>.74</i>
D.I.	<i>.04</i>	<i>.20</i>	<i>-.18</i>	<i>.13</i>	<i>-.24</i>	<i>.43</i>	<i>-.43</i>	<i>1.00</i>
<b>Granite Mountain Porphyry (N, 27)</b>								
Cl	<i>-0.17</i>	<i>-0.10</i>	<i>0.38</i>	<i>-0.24</i>	<i>0.17</i>	<i>0.23</i>	<i>0.14</i>	<i>-0.32</i>
F	<i>.43</i>	<i>.05</i>	<i>-.75</i>	<i>.65</i>	<i>-.65</i>	<i>-.17</i>	<i>.22</i>	<i>.56</i>
D.I.	<i>.38</i>	<i>.25</i>	<i>-.66</i>	<i>.47</i>	<i>-.76</i>	<i>-.26</i>	<i>.29</i>	<i>1.00</i>
<b>All rock types (N, 78)</b>								
Cl	<i>0.42</i>	<i>-0.59</i>	<i>-0.52</i>	<i>0.77</i>	<i>-0.65</i>	<i>0.42</i>	<i>0.04</i>	<i>-0.47</i>
F	<i>-.30</i>	<i>.49</i>	<i>.06</i>	<i>-.46</i>	<i>.54</i>	<i>-.39</i>	<i>-.10</i>	<i>.69</i>
D.I.	<i>-.28</i>	<i>.60</i>	<i>.24</i>	<i>-.47</i>	<i>.53</i>	<i>-.53</i>	<i>-.06</i>	<i>1.00</i>

\* All Fe calculated as FeO.

TABLE 14.—Partial correlation matrices of hornblende chemistry and rock differentiation index  
[Italic figures represent correlation at less than 95-percent confidence level, N, number of observations in a population]

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO*	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	D.I.
<b>Tortilla Quartz Diorite (N, 8)</b>								
Cl	<i>0.94</i>	<i>-0.97</i>	<i>0.96</i>	<i>-0.91</i>	<i>0.85</i>	<i>-0.96</i>	<i>-0.95</i>	<i>-0.96</i>
F	<i>.16</i>	<i>-.12</i>	<i>-.07</i>	<i>.08</i>	<i>-.01</i>	<i>-.12</i>	<i>-.01</i>	<i>-.07</i>
D.I.	<i>-.17</i>	<i>.99</i>	<i>-.99</i>	<i>.96</i>	<i>-.92</i>	<i>.99</i>	<i>.98</i>	<i>1.00</i>
<b>Rattler Granodiorite (N, 28)<sup>1</sup></b>								
Cl	<i>-0.66</i>	<i>0.76</i>	<i>0.49</i>	<i>-0.59</i>	<i>-0.35</i>	<i>0.46</i>	<i>0.40</i>	<i>0.59</i>
F	<i>.28</i>	<i>-.32</i>	<i>-.10</i>	<i>.19</i>	<i>.49</i>	<i>-.46</i>	<i>-.72</i>	<i>.28</i>
D.I.	<i>.48</i>	<i>-.55</i>	<i>-.13</i>	<i>-.27</i>	<i>.32</i>	<i>-.81</i>	<i>-.24</i>	<i>1.00</i>
<b>All rock types (N, 46)<sup>2</sup></b>								
Cl	<i>-0.35</i>	<i>0.32</i>	<i>0.50</i>	<i>-0.52</i>	<i>-0.17</i>	<i>0.03</i>	<i>-0.15</i>	<i>0.59</i>
F	<i>.28</i>	<i>-.31</i>	<i>-.13</i>	<i>.20</i>	<i>.13</i>	<i>-.36</i>	<i>.04</i>	<i>.28</i>
D.I.	<i>.24</i>	<i>-.32</i>	<i>.29</i>	<i>-.14</i>	<i>.19</i>	<i>-.70</i>	<i>-.31</i>	<i>1.00</i>

\* All Fe calculated as FeO.

<sup>1</sup> N for Na<sub>2</sub>O is 6, N for K<sub>2</sub>O is 22.

<sup>2</sup> N for Na<sub>2</sub>O is 24, N for K<sub>2</sub>O is 22.

#### Cl, F, and H<sub>2</sub>O+ contents of the rocks

The amounts of Cl and H<sub>2</sub>O+ (figs. 11A, 12C) contributed to the rocks by the hydrous igneous minerals decrease with decreasing age and increasing differentiation index of the rock, whereas the amount of F contributed decreases only in the aplitic differentiates of the stocks (fig. 12B; table 10). These figures were constructed using the mineral analyses, measured rock specific gravities, assumed mineral specific gravities, and modal abundances of the minerals (including their pseudomorphic alteration products) and ignoring the secondary hydrous phases formed in the anhydrous silicates. The trends therefore do not necessarily reflect the actual amount of original Cl, F, or H<sub>2</sub>O+ in

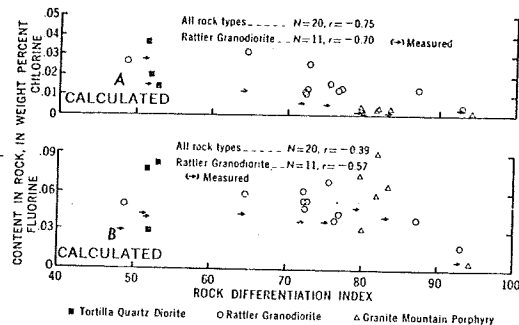


FIGURE 11.—Variation of Cl and F contents of rock samples with differentiation index. Symbols represent calculated values; arrows represent measured amount in water-leached rock powders.

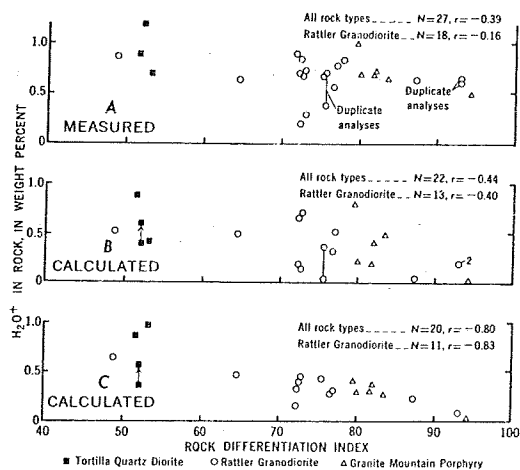


FIGURE 12.—Variation of  $H_2O^+$  contents of rock sample with rock differentiation index. A, Measured. B, Corrects A by removing effects of alteration products. C, Calculated from rock and mineral densities, mineral analyses, and modal abundance of originally unaltered igneous minerals.

the magmas because of the possibilities (1) that some of the alteration products of the igneous minerals are deuteric and thus drew halogens and water from the melt or (2) that halogens or water were either gained by or lost from the magma or rock, although for F experimental work suggests that little F would leave the magmas via an aqueous phase (Burnham, 1967).

Also plotted, as horizontal arrows, in figures 11A and 11B (data in table 15) are whole-rock analyses of Cl and F in finely ground, water-leached splits (to remove salts deposited from ground water) of a few

TABLE 15.—Cl and F contents of some Laramide igneous rocks near Ray porphyry copper deposit

Rock type	Sample No.	Contents (weight percent)			F		
		Cl (a)	Cl (b)	Cl (c)	F (b)	F (c)	F (e)
Tortilla Quartz Diorite.	17-28	0.058	0.028	0.037	0.039	0.042	0.077
Rattler Granodiorite.	17-1	.048	.015	.020	.027	.040	.029
Granite Mountain Porphyry.	46-99B	—	—	0.027	0.026	0.030	0.050
	60-113D	0.085	0.015	.035	.039	.042	.080
	T16-630	.023	.012	—	.049	.052	—
	61-25	.036	.006	.013	.037	.036	.064
	46-11G	.019	.005	.016	.032	.038	.068
Granite Mountain Porphyry.	46-11A	.050	.003	.004	.006	.007	.018
	RB5	0.023	<0.001	0.004	0.019	0.032	0.070
	GM6G	.14	<.001	.003	.039	.040	.068

a Chemical analysis by R. Moore and J. Budinsky.  
 b Whole-rock split ground to -325 mesh, leached with distilled water, dried at 40°C, and reanalyzed. A slight increase in the amount of F may reflect contamination by laboratory dust not completely compensated by blanks run simultaneously. Analysts, R. Moore and J. Budinsky.  
 c Amount of Cl and F in the rock contributed by original igneous minerals (calculated using modal data and electron-microprobe mineral analyses).

selected samples. These measured values confirm the trends (or lack of them) in figure 11 determined by calculation. However, the measured values are less than the calculated values for the halogen contents of the rock (except for F of sample 17-1, table 15). This discrepancy is expected for Cl because the OH-bearing alteration minerals of biotite contain less Cl than the biotite (fig. 13), and the loss of Cl cannot be wholly compensated by the Cl that might occur in alteration products of the feldspars (table 8). On the other hand, because the F content of some of the biotite alteration products is considerably greater than the host biotite (fig. 13), the higher values of  $F^c$  versus  $F^b$  (see footnote explanations in table 15) were not expected. It is not known if the higher values ( $F^c$  in table 15) are

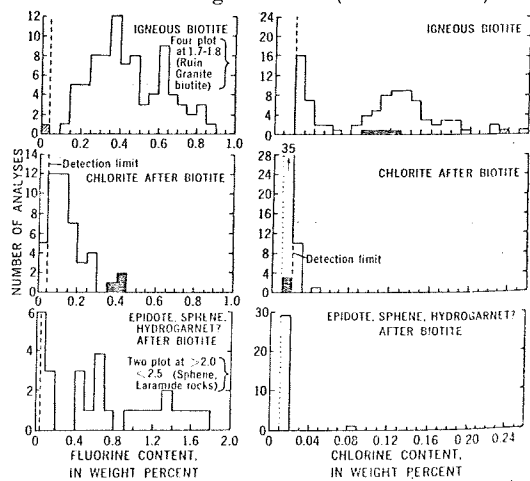


FIGURE 13.—Frequency distribution of F and Cl of biotite and biotite alteration products.

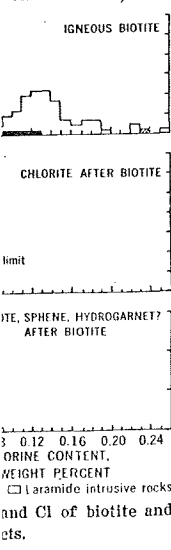
amide igneous rocks  
deposit

Weight percent)	F		
	(*)	(b)	(c)
0.039	0.042	0.077	
0.037	0.040	0.029	
0.026	0.030	0.050	
0.039	0.042	0.060	
0.049	0.052	0.063	
0.037	0.036	0.063	
0.032	0.036	0.068	
0.006	0.007	0.018	
0.049	0.052	0.070	
0.039	0.040	0.066	

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cannot be wholly  
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biotite alteration  
n the host biotite  
rsus F<sup>b</sup> (see foot-  
not expected. It is  
in table 15) are



artifacts of different analytical procedures, or whether part of the biotite's F (like the Cl) was removed from the rock during conversion of the biotite to alteration minerals.

Rock powders of all the samples were analyzed for H<sub>2</sub>O+ (fig. 12A), and although these values also correlate negatively with rock differentiation index, the correlation is poorer than for the calculated values of H<sub>2</sub>O+ (fig. 12C, table 10). The poor correlation between figures 12A and 12C is somewhat improved by removing (by calculation) the effects of the hydrous alteration products in the samples (fig. 12B), and part of the remaining wide scatter in the points (fig. 12B) may be attributed to the more inhomogeneous distribution of the hydrous alteration products (containing as much as 12 percent H<sub>2</sub>O+ by weight) compared to the hydrous igneous minerals (containing no more than 4 percent H<sub>2</sub>O+ by weight). The arrow between the two filled squares (Tortilla Quartz Diorite, fig. 12B, C) represents the original H<sub>2</sub>O+ content of sample 17-1, assuming that the fibrous amphibole (table 8) is (1) not igneous and replaces pyroxene (lower position) or (2) igneous or replacing hornblende (upper position). The statistics (table 10) were calculated assuming the former.

Simonen (1948), working with another consanguineous rock sequence, notes that more mafic rocks are richer in Cl than more silicic ones, and the data in Dodge and others (1968) show that rock Cl and F contents generally decrease with increasing differentiation index of the samples from the Sierra Nevada batholith. Thus, the findings at Ray are not unique. On the other hand, many conflicts are found in the literature. Correns (1956) found no correlation between the halogen contents and SiO<sub>2</sub> contents of rocks when comparing samples from widely separated localities, where Goldschmidt (1954) and Simonen (1948) suggest that rock F contents increase with magmatic evolution of igneous series. Kuroda and Sandell (1953) and Correns (1956) found no correlation between rock composition and Cl content, whereas Behne (1953) suggests that felsic rocks contain more Cl than basic ones. It is suspected that some of these conflicts and exceptions to the findings at Ray may result in part from comparison of data compiled for rocks of differing origins, conditions of emplacement, and degrees of alteration. For example, the data in Simonen (1948) for petrochemically related rocks show, like the Ray rocks, little or no relation between rock chemistry and F content. Similarly, if plots like figure 11A and B had been made comparing the calculated Cl and F contents of the Ruin Granite at Ray (a Precambrian quartz monzonite) with those of the Granite

Mountain Porphyry (an Early Tertiary granodiorite), there would have resulted a strong positive correlation of the contents of Cl and F in the rock with increasing SiO<sub>2</sub> content of the rocks. Clearly, because the Ruin Granite was emplaced as a batholith 1.4 b.y. prior to the Granite Mountain Porphyry (a stock), such plots would exceed their intended use. Thus the likelihood of constructing misleading geochemical trends for minor elements seems large if, in addition to a lack of time-space proximity of the rocks compared, the data are not corrected for the halogens and water introduced or lost during incipient alteration of the rock (fig. 13) or the halogens present in fluid inclusions and in salts deposited from ground water along microfractures (see table 15).

APPLICATION TO PETROLOGIC MODELS

The preceding data indicate that the abundances of the halogens and water in the igneous minerals studied have not been uniformly homogenized nor are they detectably controlled by changes in chemistry of the minerals, proximity or degree of local alteration, or potential susceptibility of a grain to exchange with the magma(s) or aqueous fluids. On the other hand, changes in abundance of Cl, F, and calculated H<sub>2</sub>O+ in the igneous hydrous minerals appear to be related to changes in the age and chemistry of the parent magma(s). Similar trends are observed for minerals in other consanguineous igneous suites. These facts suggest that the hydrous igneous minerals studied at Ray probably retain an imprint of magmatic events and that the changes in the halogen and water contents of the minerals are more likely the result of changes in or initial differences between the magma(s) than the result of postmagmatic events. This interpretation is consistent with the resistance of fluorapatite to exchange with chloride-rich aqueous fluids (Ekström, 1973).

Given the interpretation that the changes in mole fractions of Cl, F, and H<sub>2</sub>O (X<sub>Cl, F, H<sub>2</sub>O</sub>) in the minerals probably reflect magmatic processes during development of the igneous suite at Ray, it is of interest to petrology and current ideas about ore genesis if the data lead to the determination of how X<sub>Cl, F, H<sub>2</sub>O</sub> varied in the melt(s) as the magmas became younger and more differentiated. Unfortunately, such a determination requires experimental data not yet available concerning the activity coefficients of Cl<sup>-</sup>, F<sup>-</sup>, and OH<sup>-</sup>, how the activity coefficient of each ion changes relative to the others with respect to temperature and pressure, and if and how the partition coefficients (between melt and mineral) of each ion change with temperature and pressure. Additionally, subjective deci-

sions must be made as to whether the exposed plutons represent (1) sequential differentiates of one batholith while it was emplaced in the upper crust, (2) differentiates of several common source batholiths while they were emplaced in the upper crust, (3) as in 1 but occurring in the lower crust or upper mantle, (4) as in 2 but occurring in the lower crust or upper mantle, or (5) sequential or separate partial melts from a common source area.

It seems obvious that with so many possible variables, strong defense of any unique explanation for the data would be unwise. If explanations 2, 4, or 5 apply to Ray, then data need not be necessarily considered petrologic indicators of processes in differentiation of magma. However, the data for one magma (Rattler Granodiorite) are consistent with those for the entire igneous suite and, as cited earlier, with similar data for other igneous suites. Thus it seems at least reasonable to postulate that the trends observed in figures 8-10 could result from differentiation of a single magma and that evaluation of the magmatic behavior of Cl, F, and H<sub>2</sub>O is warranted. The following discussion concerns only explanation 1 above because of its significance to one current theory of ore genesis—that both ore and ore fluid components for porphyry copper deposits have their source in calc-alkaline magma emplaced in the upper crust.

A long list of literature, reviewed in part by Lowell and Guilbert (1970), notes a time-space relation between intermediate calc-alkaline intrusive rocks and "disseminated" or porphyry copper ore deposits; this relation has generally been interpreted as causal. In the classical magmatic hypothesis of ore deposits, the calc-alkaline magmas are considered the vessels that transported the copper and sulfur to or near to the deposits, and there the magmas produced the mineralization through differentiation. However, in the Laramide plutons associated with Ray and also in those elsewhere in Arizona (Rehrig and Heidrick, 1972), mineralization is associated with a regional tectonic fracture system rather than with observed radial, concentric, and sheeting joints associated with cooling of the plutons. Thus, if the mineralizing fluids evolved according to the classical magmatic model, they must have come from deeper sources than the exposed plutons; that is, explanation 1 above, in which water is first concentrated through crystal differentiation in and later released from a nearby batholith. To facilitate transport of the ore and to explain the NaCl in fluid inclusions in porphyry deposits, the fluids released should preferably be rich in chloride (see for example, Helgeson, 1964; Garrels, 1941; Roedder, 1971).

This presumed late buildup of Cl and H<sub>2</sub>O was not recorded by the minerals in the exposed plutons associated with Ray (figs. 8-10, table 10). Thus, either the classical magmatic hypothesis does not apply to the Ray deposit, or it must be postulated that the minerals did not record the required processes in the batholith. Three models that might explain the data are presented below. The first two outline the processes and list the special conditions that apply if the rocks studied here are related to a nearby batholith that produced mineralizing fluids. The third model does not assume a classical magmatic origin for the Ray deposit.

#### Changes imposed on the stocks

If the classical magmatic hypothesis applies to Ray and if figures 8-10 depict directly how  $X_{Cl, F, H_2O}$  varied in the melts of the exposed stocks, then the processes in the stocks did not follow those in the parent batholith. Because the stocks were emplaced at shallower depths than the batholith, it seems a reasonable postulate that they evolved water before the batholith did. Experimental studies (Koster van Groos and Wyllie, 1969; Wyllie and Tuttle, 1964) indicate that in a degassing melt, Cl would leave with H<sub>2</sub>O while most of the F would tend to remain in the melt (Burnham, 1967; Munoz and Eugster, 1969). Thus evolution of water from the ascending and crystallizing magmas of the exposed stocks would increase the activity of F in the melts of the stocks relative to the fugacity of water and the activity of chlorine while the batholith could continue to maintain and concentrate chlorine and water. However, several lines of evidence have already been discussed that are not consistent with the assumption that the exposed stocks saturated early in their crystallization history or evolved much water. To review, these are that: (1) biotite does not show a magnesium enrichment with decreasing age or with progressive differentiation of the stocks, (2) the percentage of aplites in the stocks is low, (3) pegmatitic aplites are sparse, (4) metamorphic aureoles around the intrusive rocks, both stocks and dikes, are restricted and in some places are virtually absent even in carbonate terrane, (5) micro-litic features or cavities have not been identified in field exposures or thin section samples of the Laramide stocks, and (6) the fluid inclusions in quartz in the rocks are sparse, two phase, and homogenize at temperatures considerably below the granite minimum. Also problematical to the postulate that evolution of Cl-bearing water explains the correlations of  $X_{Cl, F, H_2O}$  in the minerals with rock chemistry and age are ex-

and H<sub>2</sub>O was not proposed plutons as 10). Thus, either does not apply to ated that the min- processes in the explain the data tline the processes apply if the rocks by batholith that third model does rigin for the Ray

sis applies to Ray y how  $X_{Cl, F, H_2O}$  d stocks, then the allow those in the were emplaced at it seems a reason- water before the (Koster van Groos le, 1964) indicate d leave with H<sub>2</sub>O remain in the melt ster, 1969). Thus ing and crystalliz- would increase the cks relative to the of chlorine while intain and concen- r, several lines of ssed that are not the exposad stocks ization history or these are that: (1) n enrichment with e differentiation of plites in the stocks sparse, (4) meta- rusive rocks, both in some places are terrane, (5) miaro- been identified in les of the Laramide s in quartz in the omogenize at tem- granite minimum. e that evolution of lations of  $X_{Cl, F, H_2O}$  ry and age are ex-

perimental data (Munoz and Ludington, 1974; Munoz and Eugster, 1969). These data suggest that evolution of water at magmatic temperature from the stocks in amounts proportional to those required of the parent batholith to form the Ray deposit should have resulted, but did not (table 4), in (1) homogenization of F contents of biotite in individual samples and stocks and (2) higher F contents in the high-temperature igneous rather than in the lower temperature hydrothermal biotite. The fact that neither expectation is met requires that the igneous biotite had little contact with the water evolved at magmatic temperature and that the ore fluids had chemical parameters different from the water evolved from the stocks. In addition, the increase in F content of the biotites with increasing differentiation (fig. 9) is opposite to the trend expected because with vapor phase present, each of the following factors should have resulted in a decrease in the F content of biotite: (1) the Mg content of the biotite decreases with differentiation (see Ludington, 1973; Ekström, 1972; Munoz and Eugster, 1969; Munoz and Ludington, 1974; Wones and Eugster, 1965), (2) the F content of the rock decreased or remained the same during differentiation (fig. 11B; see also Munoz and Eugster, 1969), and (3) presumably the temperature of the differentiating magma(s) and its evolving vapor phase(s) would be progressively lower (see Munoz and Eugster, 1969). Thus, an additional requirement on the evolving water(s) is that they became progressively enriched in F as the host rock became more felsic despite the observed decrease of F content of the rock (fig. 11B) and probable decrease in temperature of the magma. As an alternative to this, it could be postulated that the Tortilla Quartz Diorite and Rattler Granodiorite did not evolve much water whereas the Granite Mountain Porphyry evolved much more water that, for some reason, resulted in higher contents of and homogenization of F in individual biotite grains of the Granite Mountain Porphyry without homogenizing the grains with respect to the other elements or with respect to F contents of biotite in adjacent grains and in other samples from the stock. Finally, at their depths of emplacement, the stock should have saturated at between 2.5 to more than 3.5 wt percent H<sub>2</sub>O (Burnham, 1967); this is about the approximate amount required in the melts for biotite to form in the stocks (D. R. Wones, oral commun., 1974; Wones and Dodge, 1966). Thus, if it is postulated that the magmas evolved water while ascending or during the main stage of crystallization, disequilibrium crystallization also must be postulated.

Taken alone, any one of the foregoing requirements and observations does not preclude the possibility that the character of the magmas of the stocks changed through evolution of water and chlorine. However, with so many requirements on the presumed aqueous phase(s) and with the popular desire for simplicity and consistency in interpretation of data, alternative explanations of the trends with age and chemistry indicated in figures 8-10 seem warranted. Another model that maintains the assumptions of the classical magmatic model is given below.

#### End-stage degassing of the stocks and batholith

This model drops the requirement that the stocks evolved water during their ascent and main-stage crystallization but maintains the requirement of the classical magmatic model that chloride-rich water was produced at or near the end of differentiation of the parent batholith (and also of its effluent stocks). However, like the preceding one, this model finds the same problems with the paucity or even negative physical evidence that water in the volumes proportional to those required for the deposit evolved from the stocks at magmatic temperatures. It also requires the same special conditions to explain the lack of magnesium enrichment in biotite from aplites of the stocks and why the biotite did not respond chemically to presence of the evolving magmatic water. In addition, the failure of  $X_{Cl, H_2O}$  in the minerals to record the buildup of  $X_{Cl, H_2O}$  in the parent batholith means that to explain figures 8-10, changes in the activities of Cl<sup>-</sup>, F<sup>-</sup>, and OH<sup>-</sup> (or fugacity of H<sub>2</sub>O) in the melt do not directly record changes in  $X_{Cl, F, H_2O}$  in the melt. This model cannot be evaluated further without experimental data that indicates that activity of F can in fact increase relative to the activities of both water and chlorine in a differentiating melt while  $X_F$  in the melt (probably very close to figure 11B) remains roughly constant or decreases and while  $X_{Cl}$  and  $X_{H_2O}$  in the melt increase.

#### Magmatic evolution through crystal differentiation

This model postulates that the magmas were undersaturated in water when emplaced at the present levels of exposure, that the precipitation of hydrous minerals controlled the activities of Cl, F, and H<sub>2</sub>O in the melt, and, as a consequence of these postulates and the petrologic evidence indicating that the hydrous minerals continued to form late in the crystallization history of the stocks, that the magmas evolved very little water. The paucity of evolved water is consistent with fluid-inclusion data, lack of miarolitic features in

stocks, paucity of pegmatitic dikes, low percentage of aplites, lack of Mg enrichment in the igneous biotite, and restricted skarn development associated with the plutons. It is also consistent with the F chemistry of the biotite. This interpretation of the data does not preclude the possibility that water evolved from the magmas after the hydrous minerals ceased forming, perhaps after other components required for formation of the hydrous minerals were consumed or perhaps in response to local disequilibrium. In fact, the presence of interstitial epidote in the stock suggests that fugacity of  $H_2O$  in the stocks did increase locally during the very final stages of crystallization. However, in this model the water evolved was probably small in amount and low in Cl content.

If the magmas were originally undersaturated and evolved only insignificant amounts of water relative to the total volumes of the stocks, then the trends observed between the age and chemistry of the rock and the abundances of Cl, F, and  $H_2O$  in the minerals (figs. 8-10) must be explained by crystal differentiation, whereby most of the Cl, F, and  $H_2O$  originally present in each magma was extracted from the melts by the hydrous minerals. In this model then, changes in activities of  $Cl^-$ ,  $F^-$ , and  $OH^-$  (as indicated in figs. 8-10) were proportional to changes of  $X_{Cl^-}, F^-, OH^-$  in the melt (as indicated in figs. 11A, B; 12C). Thus, for the Rattler Granodiorite, the first hydroxyl-bearing minerals that separated from the magma tended to incorporate more chlorine relative to water and fluorine, and more water relative to fluorine than hydroxyl-bearing minerals that separated at a later time or from the more differentiated magma. If all the stocks came from the same nearby batholith (questionable that it would remain molten for 10 m.y. in the shallow crust) or deep batholith (where heat input might lengthen the life of the batholith), then the explanation applied to the Rattler Granodiorite applies to the entire igneous suite.

As with the preceding model, there is no direct experimental justification or refutation for this explanation of the data. However, F is much more soluble in silica-rich melts than both  $H_2O$  and Cl, and  $H_2O$  is more soluble than Cl (Koster van Groos and Wyllie, 1968, 1969; Burnham, 1967). Thus given the assumption that less soluble components would tend to leave the melt prior to more soluble components, this model, although not irrefutably supported, is at least consistent with the experimentally determined relative solubilities of Cl, F, and  $H_2O$  in silicate melts.

Failure of the outer edges of the mineral grains consistently to record the postulated progressive depletion of Cl and  $H_2O$  in the melts relative to F may be at-

tributed to (1) inhomogeneities in the melt, (2) convective mixing of the grains; or, (3) in-place variations of conditions controlling halogen uptake. The first of these alternatives is favored because it seems likely that with several coexisting hydrous phases simultaneously consuming volatiles from the melt in different amounts and at different rates, and with the nearby anhydrous minerals simultaneously rejecting and thus reconcentrating them at different rates, it seems reasonable to postulate that the diffusion rates of all components were not adequate to maintain, on a local scale, a homogeneous melt with respect to Cl, F, and  $H_2O$ . The larger intragrain and intrasample variation of Cl and F in apatite relative to the biotite, hornblende, and sphene might also be explained by inhomogeneities in the melts because the demands by apatite for Cl and F in the melt were greater and thus less likely to be fulfilled at a consistent ratio of Cl:F: $H_2O$  compared to those of the hydrous silicates. The two alternative explanations offered above do not seem as likely because one should expect the biotite, hornblende, and sphene to have recorded variations in halogen abundances similar to those observed in the apatite, if either convective mixing or in-place variation of  $P_{H_2O}$ ,  $T$ , or  $P_{total}$  were the major cause of the observed intrasample and intragrain variations. Further, it is difficult to visualize mechanisms that would change  $P_{H_2O}$ ,  $T$ , and  $P_{total}$  on a millimetre scale or ways in which adjacent grains might have moved over the distances required to cause the observed differences in halogen contents, both within and between grains, in the samples that were possibly 50-80 percent crystallized prior to formation of hydrous minerals.

This model requires that the melts arrived at their level of emplacement not only undersaturated but carrying not much more than 1-0.5 percent  $H_2O$  by weight (mafic and felsic stocks, respectively), or in other words, the hydrous minerals could not begin to form in the magmas until about 50 percent of the mafic magmas, and about 80 percent of the felsic magmas had crystallized. This is consistent with petrologic observations and interpretations for most of the samples but not with those for the rhyodacite dikes and the porphyritic facies of the Rattler Granodiorite where the presence of phenocrysts suggests the possible onset of hydrous mineral formation when less than 30-50 percent of the magma(s) had crystallized. Thus, if the above model is to explain the data, either some of the magmas (and part of the Rattler Granodiorite magma) had two to three times more water initially, or water was locally concentrated in or introduced into some of the magmas. For example, the porphyritic facies of the Rattler Granodiorite may have gained water from the



rest of the melt because of diffusion of water to cooler parts of the melt (Kennedy, 1955), thereby enriching one part of the melt in water at the expense of the other prior to formation of the groundmass minerals. However, under conditions of small concentration gradients, diffusion of water in melts may be slow (Burnham, 1967), and instead, a convecting or turbulent part of the magma exposed to wet wallrocks may have stripped water from the wallrocks in a manner similar to metallurgic zone refining (Shaw, 1972; Harris, 1957). A final special condition required for this model concerns sample 60-113D (D of figs. 8-10), a dike that intrudes both the porphyritic and nonporphyritic facies of the Rattler Granodiorite prior to development of aplites in the stock. Biotite and hornblende in this dike contain more Cl than biotite and hornblende in rocks cut by the dike. Possible explanations for this relation are (a) turbulent flow in the dike caused "stripping" of Cl and H<sub>2</sub>O of meteoric or magmatic origin from the nearly crystallized parts of the stock, (b) the dike represents a late resurgence from an unconsolidated deeper and less differentiated part of the stock or (c) the dike represents an intrusion that was not part of the Rattler Granodiorite magma.

#### Concluding remarks

The last of the three models discussed in this section is thought to be consistent with more data and to require fewer unprovable special conditions than the first two models, but no one model can be considered the unique explanation of the data, particularly if all stocks and dikes did not originate from a nearby batholith. Although the first two models do not incorporate all the field, chemical, and existing experimental observations as favorably as the last, neither they nor a classical magmatic genesis for Ray can be ruled out with certainty. On the other hand, the data for the Ray rocks neither require nor support the classical magmatic origin of the Ray deposit, and they are similar to those for plutons that are not associated with porphyry copper deposits. Thus a source alternative to an upper crustal batholith might profitably be sought to explain the mineralization at Ray and perhaps other deposits.

#### BIOTITE AS A PARTIAL OR SUPPLEMENTARY SOURCE OF CHLORINE AND FLUORINE IN THERMAL WATERS

##### Chlorine

The distribution of Cl between igneous biotite and its propylitic type alteration products at Ray (fig. 13) suggests that natural thermal waters and ore fluids

might find a partial or supplementary source of Cl in that released during alteration of biotite to chlorite, epidote, and sphene. For example, upon alteration of 20 percent of the biotite (comprising an average of more than 7 volume percent of the rock), each cubic kilometre of average Laramide igneous rock ( $\rho \approx 2.8$  g/cm<sup>3</sup>) at Ray, using the average Cl abundance of biotite (1,100 ppm) analyzed here, would release as much as  $4 \times 10^{10}$  g Cl to the altering fluid if the average biotite alteration product contained Cl in amounts just below detection (200 ppm). If the average alteration product contained Cl in amounts considerably below detection levels (contents of 20-30 ppm),  $4.8 \times 10^{10}$  g Cl would be released to the fluids.

This does not imply that the major source of Cl in natural hot waters is altered biotite because much might be trapped in fluid inclusions or in alteration products of the feldspars. For example, if the observed modal phengite and clay (both containing no more than 200 ppm Cl) had developed in the coexisting plagioclase and K-feldspar during the period of biotite destruction, only  $1.3 \times 10^{10}$  to  $1.8 \times 10^{10}$  g/km<sup>3</sup> Cl would still be available for incorporation in fluid inclusions or for further transport in the fluid phase. This does not rule out the possibility that alteration of biotite might be a supplementary or partial source of Cl in hydrothermal fluids, particularly if the hydrous alteration products of plagioclase contain significantly less Cl than that detectable by methods used here (200 ppm) or if the plagioclase alteration occurred at a different time than the biotite alteration.

##### Fluorine

Chloritization of the igneous biotite in the Laramide rocks at Ray was accompanied by development of anhedral sphene, epidote, and perhaps even the F-bearing hydrogarnet(?) (in decreasing order of abundance). The sphene and hydrogarnet(?) contain F in abundances usually greater than the host biotite (fig. 13, compare tables 4 and 8) suggesting that much of the F in the biotite was immediately reprecipitated. However, if data in table 15 apply, only part of the F originally in the biotite remained in the rock (compare F<sup>b</sup> with F<sup>c</sup> in table 15). Thus, it seems possible that biotite could also provide some F to waters that cause propylitic alteration, particularly in instances where the calcium content of the waters is low, and epidote and sphene do not form in biotite during the alteration.

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