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MAGMATIC BEHAVIOR OF Cu, S, Cl, F, AND H₂O IN IGNEOUS ROCKS

ASSOCIATED WITH THE RAY PORPHYRY COPPER DEPOSIT, ARIZONA

Presented at A.I.M.E. Field Conference,

Ray, Arizona, April 16, 1977

By

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Porphyry copper deposits are the subject of a large volume of literature indicating that controversy still reigns as to which model or combination of models explains their origin, and yet, over 70 years ago we reached agreement that the well-documented space-time relationship between the deposits and calc-alkaline plutons indicates a genetic tie between them. This genetic tie is generally assumed to indicate a causative role for an exposed or nearby hidden pluton. There are many variants, but the two end-member models that incorporate this causative assumption are the meteoric water model and the orthomagmatic model. It is my opinion that the controversy originates from use of indirect data and variant models to explain new observational data and experimental studies that threaten the survival of the basic end-member models. One of many examples of this is the end-stage magmatic evolution of chlorine-rich water required of the orthomagmatic model. This evolution is required because the low copper content of calc-alkaline plutons demands a large source magma, that, because it generally is not visible, has to be buried. Additionally, much of the ore minerals in porphyry deposits is along fractures. Both conditions require transportation of the ore components from the magma, and to transport enough ore components, given the limited amount of water soluble in a melt and the low solubility of base-metal sulfides in water without benefit of chloride complexing, we required of the original Lindgren magmatic model that the source pluton produced chloride-rich water. However, we did not investigate the rocks associated with deposits to substantiate the hypothesis. We went to the laboratory and found that sufficient water and chlorine could be dissolved in silicate melt in a gold capsule in a high-pressure high-temperature bomb to allow postulation of sufficient water and chlorine in the stocks associated with porphyry deposits; in other words, we invested in indirect rather than direct studies.

Lest it appears that I have unfairly singled out the orthomagmatic model in this example, I have similar anecdotes concerning the meteoric water model, but in the interest of time, just the data from the rocks at Ray that comment upon it unfavorably will be presented here. Several years ago it was found through comparison of the sulfur content of biotite in Laramide rocks at Ray, Laramide rocks at Esperanza, and Precambrian basement rock around Ray with the sulfur content of alteration products of the biotite, that sulfur was removed from the rock during the biotite alteration (fig. 1). These data not only indicate that the sulfur content of whole-rock and mineral-separate analyses might be low or erratic, it suggested to me that sulfur that was isotopically indistinguishable from that supplied by a magmatic fluid could be introduced by meteoric water to a deposit (Banks, 1973). Later it was found that a release of chlorine also accompanied chloritization of biotite (fig. 2). As indicated earlier, this is an attractive feature if one is making a base-metal ore fluid with sulfur in it. However, the alteration of biotite to chlorite both at Ray and Esperanza resulted in a very large gain in copper over the precursor biotite (see fig. 3). Thus, although alteration of the igneous rocks theoretically could have provided through the medium of circulating meteoric water some of the sulfur and chlorine in the fluids that formed the Ray deposit, the same alteration provided mineralogy that would have removed, rather than introduced, copper from the fluids. This is direct evidence from the rocks that severely hampers, if not totally eliminates, meteoric water in the role as the causative agent for Ray.

A further implication of this study is shown in figure 4. The site of the strongest concentration of this secondary copper occurs at the optical and chemical boundary between chlorite and biotite. This material is probably vermiculite and contains as much as 14 weight percent CuO , concentrations that could account for all of the copper in the average whole-rock analysis if only 1 percent of the biotite was altered to this copper vermiculite. Additionally, chlorite in the rocks contains as much as 5,000 ppm copper, which could also account for the bulk of the copper in the whole-rock analyses. These data offer a good explanation of why the copper contents of rocks and biotite separates are so erratic both at Ray and elsewhere, and provide ample reason why such data are unlikely to comment on primary igneous processes. Thus the studies on the alteration of primary igneous phases in the Laramide plutons near Ray indicate that meteoric water as the causative agent for the deposit is an unlikely postulate and indicate, in addition, that alteration, even if incipient, could strongly influence the chlorine, water, and copper content of both rock samples and mineral separates. Therefore, to obtain data on the ore-fluid components that was to comment on the processes occurring in the magma that produced the stocks, the data had to be produced by in situ microanalytical techniques where the purity of the analytical spot could be assured optically and confirmed chemically, and where the analytical data could be evaluated by observing variations in the

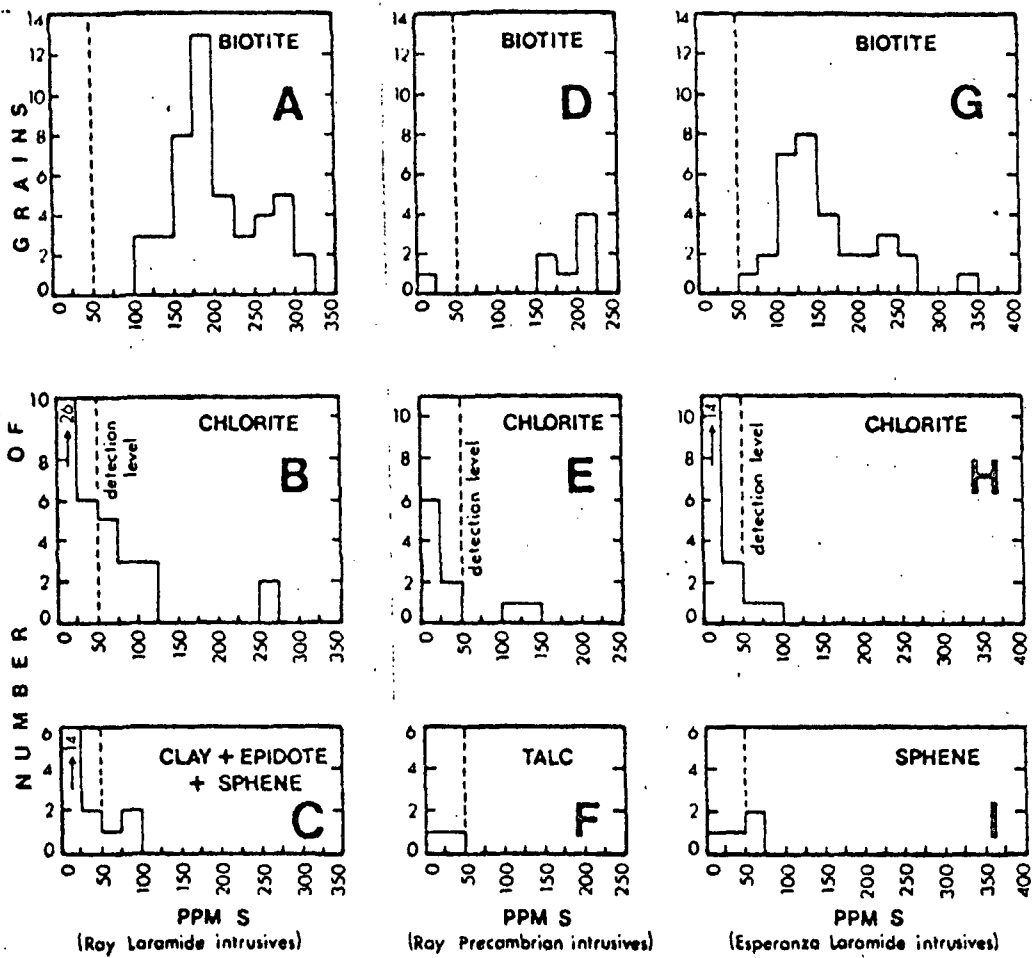


FIG. 1. Frequency distribution of sulfur in igneous biotite (A,D,G), chlorite (B,E,H), other alteration products of biotite (C,I), and talc after olivine (F) from intrusive rocks at Ray and Esperanza, Arizona (from Banks, 1973)

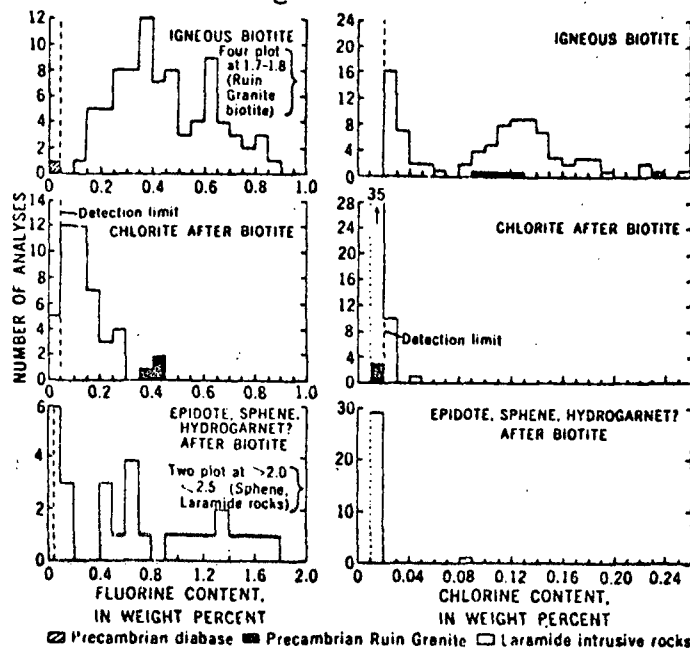


FIGURE 2.—Frequency distribution of F and Cl of biotite and biotite alteration products (from Banks, 1976)

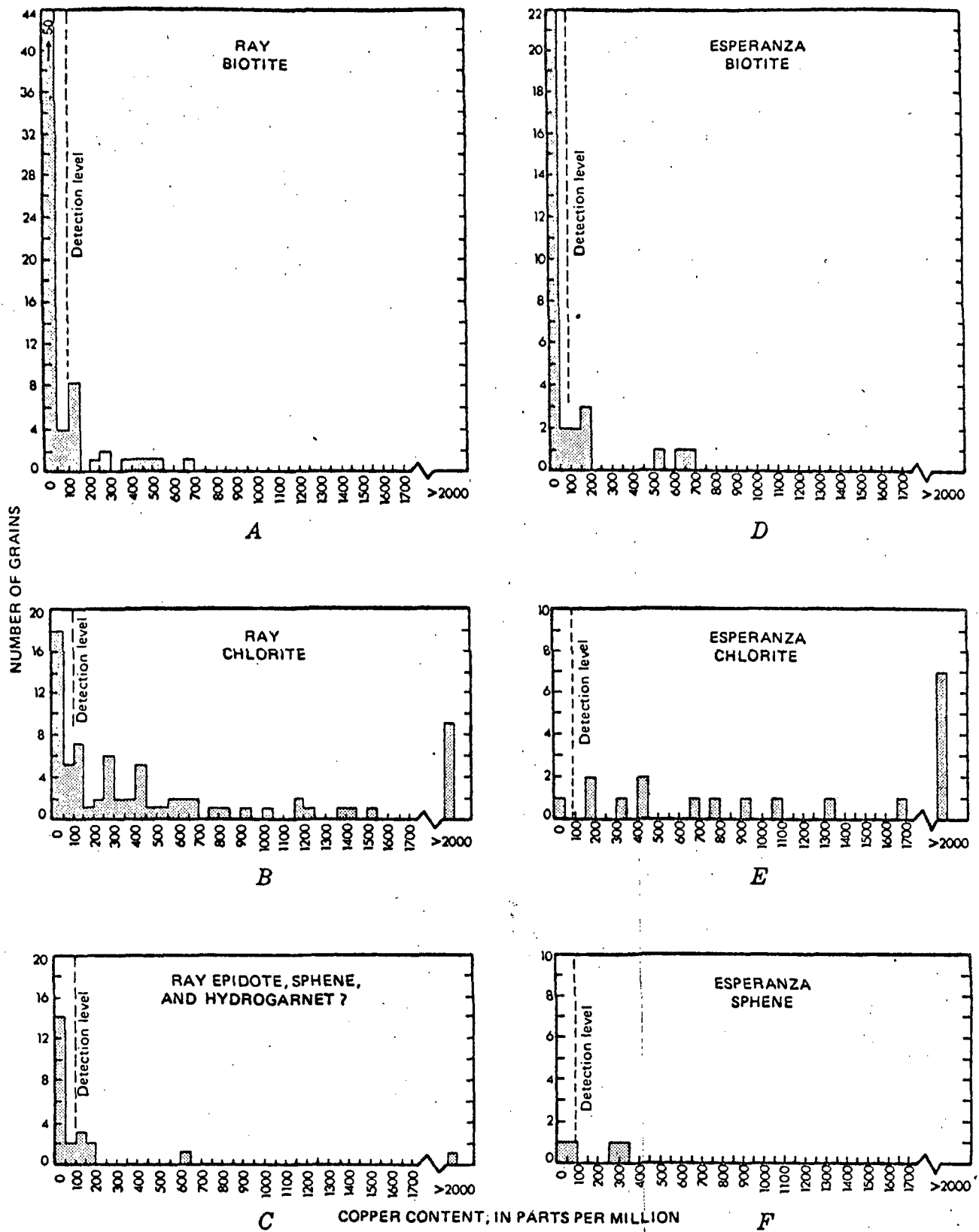


Figure 3.—Frequency histograms showing copper contents of biotite (A and D), chlorite (B and E), epidote, sphene, and hydrogarnet? (C), and Sphene (F) from Laramide intrusive rocks near the Ray and Esperanza copper deposits, Arizona. Detection levels established at three times the square root of the average background counts.

Figure from Banks (1974).

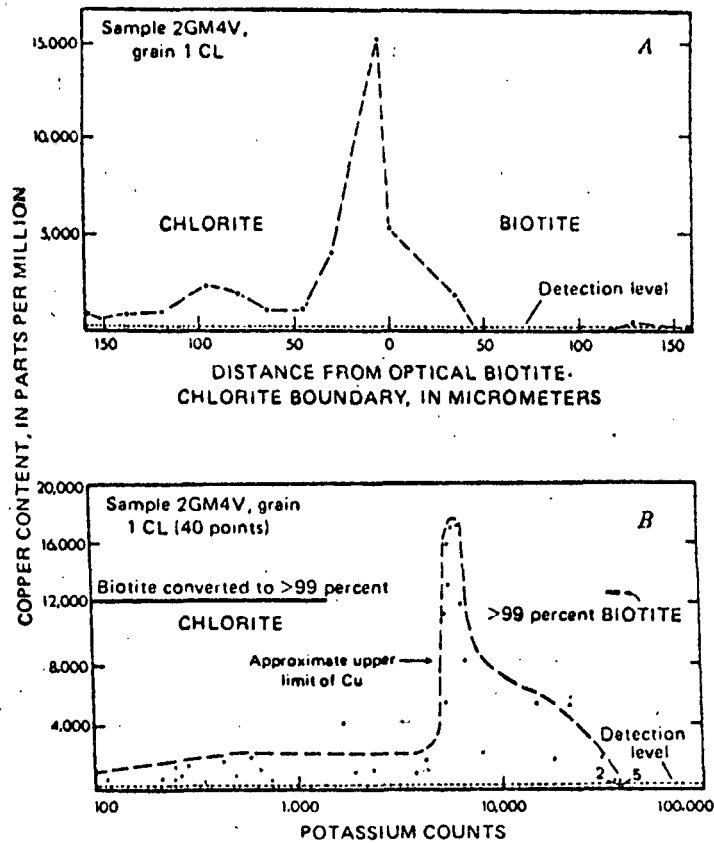


Figure 4.—Distribution of copper in biotite, chlorite, and transitional material. Bars indicate range of potassium (K) counts that designates relatively pure chlorite (<0.1 percent K_2O) and biotite (K counts equal to the average of K counts for biotite grains with no chloritization in the same mount). Counting time is 200 s, terminated on fixed beam current. Detection level was established at three times the square root of the average background counts. A, Distribution of copper in biotite and chlorite relative to the optical mineral boundary. B, Distribution of copper in chlorite, biotite, and transitional material relative to concentration of potassium. Figure from Banks (1979)

abundance of the ore-fluid components in minerals with respect to primary and secondary features in the mineral, the thin section, and the rock sample.

At this point in the work, the classical magmatic or orthomagmatic model seemed best to explain Ray, and the research then focused on this model. However, there are many variant definitions of the orthomagmatic model. Thus, to avoid misunderstanding during presentation of the data, the usage here is the end-member model--whereby either an exposed or a buried upper crustal pluton carried the ore fluid components from depth near to the deposit and in the upper crustal site produced the ore fluids by differentiation. This model was generated from the Lindgren model of in situ differentiation of ore because of an interesting history of direct observations that contradicted it and then indirect discoveries that made it again permissive. In the example given earlier, these discoveries require the evolution of chlorine-rich water, or the first four special requirements of end-member orthomagmatic model as it now stands (fig. 5). Concerning requirements 1 and 4, their partial redundancy results from the fact that the illustration was made for another talk in which I went through the historic development of the present orthomagmatic model from the original Lindgren one.

Ten years ago, we set out to gather data on the requirements listed in figure 5. We first generated the field and age data presented by Cornwall and Banks (1977). In brief review, we found that no geologic or petrologic parameters indicate that the Ray rocks are petrochemically unique when compared to similar rocks in terranes that contain no deposits, and this is a problem common to calc-alkaline series around most base metal deposits. Also presented earlier (Banks, 1976; Cornwall and Banks, 1977) were the observations that suggest that the Ray rocks were undersaturated when emplaced and that they did not evolve much water. These observations which are not favorable for a classical magmatic origin for Ray are presented for review in figure 6. Even these relationships are not unique to Ray, when compared with other porphyry copper deposits. Therefore, the fluids that are presumed to have evolved from these rocks to form the deposits are often attributed ghostlike powers of hiding their former presence from the now-solid rock. Acting on the assumption that the developing ore fluids were not as elusive to minerals that were forming from the same magma, I analysed by microprobe, the igneous minerals in 7 of the 12 intrusive rock types near the deposit, hoping that they had monitored the magmatic behavior of the components required for the ore fluid. The seven rock types are listed in geologic order in figure 7, youngest at the top. They span the entire suite with respect to age, chemistry, texture, mineralogy, and mafic minerals present. I used about 25 samples, from both dikes and stocks, but the stocks were sampled more heavily because these are least susceptible to gain, loss, or contamination with ore-fluid components. One of the stocks--the Rattler Granodiorite--provided a variation in texture, chemistry, and mineralogy that approximately span those of the entire igneous suite.

SOME REQUIREMENTS OF THE ORTHOMAGMATIC MODEL.

1. THE MAGMA CONTAINS SUFFICIENT WATER FOR SUPER-SATURATION.
2. WATER EVOLVED CONTAINS SUFFICIENT CHLORIDE FOR METAL TRANSPORT.
3. SUPERSATURATION, TRANSPORT, AND DEPOSITION OCCUR AT THE RIGHT TIME.
4. ENOUGH WATER EVOLVES TO ACCOMPLISH TRANSFERS.
5. MELT CONTAINS SUFFICIENT METAL AND SULFUR FOR THE DEPOSIT.

Figure 5.

FIELD, CHEMICAL, AND MODAL DATA THAT SUGGEST THE RAY STOCKS DID NOT SATURATE EARLY OR EVOLVE MUCH WATER

1. VOLUME OF PEGMATITE AND APLITE DIKES IS LOW
2. THERMAL AUREOLS ARE RESTRICTED EVEN IN CARBONATE HOST ROCKS EXCEPT THOSE WITH ENDOSKARN OR OTHER INDICATIONS OF WATER SOURCES OUTSIDE OF THE EXPOSED OUTCROP
3. MIAROLITIC FEATURES LACKING IN STOCKS
4. FLUID INCLUSIONS HOMOGENIZE BELOW 450°C
5. HYDROXL MINERALS ARE GENERALLY PARAGENETICALLY LATE, PARTICULARLY IN THE MORE DIFFERENTIATED STOCKS
6. AT EMPLACEMENT DEPTHS, REMOVAL OF WATER BY HYDROXL MINERAL FORMATION WAS LIKELY TO HAVE INHIBITED SATURATION OF THE MELT, EVEN DURING APLITE FORMATION
7. FE/MG CONTENT OF BIOTITE INCREASES WITH DECREASING AGE
8. MAGNETITE DECREASES IN ABUNDANCE WITH DIFFERENTIATION AND THE BULK OF IT FORMED AT ABOUT THE SAME TIME AS THE HYDROXL MINERALS

Figure 6.

Thus, by comparing the behaviors of the ore-fluid components in one melt and in all the melts of the entire igneous suite, it is possible to evaluate whether different depths of emplacement (as much as and perhaps more than 1.5 km), ages of emplacement, or rates of magma ascent might or might not have contributed to any trends that could be found.

In addition, a large number of variables were investigated to evaluate the magmatic behavior of the ore-fluid components in the melts as well as to check if the grains analyzed were affected by exchange with an aqueous phase (Banks, 1976). I analyzed centers and edges of individual grains, made traverses across grains, analyzed as many as five separate grains of the same mineral across a thin section or in several sections of the same sample, compared the contents of the ore-fluid components of phenocrysts with those of the same minerals included in groundmass or in diverse mineral hosts, compared variations in the content of these components with those of the other elements in the minerals, and compared their variations in like minerals from different samples having like whole-rock chemistry but different mineralogy, texture, and degree of alteration.

Only a brief review of part of data gathered, that pertaining to the orthomagmatic model data, is possible here. However, because of the voluminous amount of even the abstracted data, I will divide the rest of the report into three parts. The first part deals with the first four requirements of the orthomagmatic model (fig. 5), or what the rocks tell us about the behavior of the components required to cause efficient transfer of ore components from the magma to the deposit. The second will deal with petrology of the magmatic sulfide minerals that separated from the magmas, and the third will present the data for copper and sulfur in the silicate and oxide phases in the rocks. Thus, the last two parts comment on the fifth requirement of the orthomagmatic model, the behavior of copper and sulfur in the magmas. The results of the studies were surprising to us because when we started them, we expected to substantiate the orthomagmatic model. Instead, the data from the rocks strongly suggest that ore fluids could not have been produced by the upper crustal plutons exposed. In other words, the magmas probably did not produce much H₂O, the little H₂O released probably had low chloride content, and its access to even the small amount of copper and sulfur in the magmas was very restricted.

Figure 8 summarizes the findings of the microprobe study for Cl, F, and H₂O in the minerals. These statements are documented in publication (Banks, 1976), and say in essence, (A) that biotite, apatite, and hornblende contain chlorine, fluorine, and water, and that sphene contains fluorine and water, and (B) that the grains have not been homogenized with respect to the ore-fluid components. Furthermore, as in C and D, the variations in abundance of these components appear not to have been influenced by exchange with an aqueous phase because

ROCK TYPES STUDIED

ROCK TYPE	TEXTURES OF VARIOUS FACIES	MAFIC MINERALS -VARIOUS FACIES
RHYODACITE (DI=81)	PORPHYRITIC	BI-HBL
TEAPOT MOUNTAIN PORPHYRY (DI=84)	PORPHYRITIC	BI-HBL
GRANITE MOUNTAIN PORPHYRY (DI=80-95 Av=82)	GRANITOID SERIATE PORPHYRITIC PORPHYRITIC APLITIC	BI BI-trHBL
RHYODACITE (DI=80)	PORPHYRITIC	BI-HBL
RHYODACITE (DI=74)	PORPHYRITIC	BI-HBL
RATTLER GRANODIORITE (DI=48-93 Av=73)	HYPIDIOMORPHIC GRANULAR SERIATE PORPHYRITIC PORPHYRITIC APLITIC CHILLED	HBL-PX BI-HBL-PX BI-HBL HBL BI
TORTILLA QUARTZ DIORITE (DI=50)	HYPIDIOMORPHIC GRANULAR	HBL-PX BI-HBL-PX

Figure 7.

SUMMARY OF PROBE ANALYSES OF IGNEOUS MINERALS FOR CL, F, AND H₂O

- A. APATITE, BIOTITE, AND HORNBLende CONTAIN CL, F, AND H₂O, AND SPHENE CONTAINS F AND H₂O
- B. VARIATIONS IN ABUNDANCE OF CL, F, AND H₂O OCCUR BETWEEN AND WITHIN LIKE MINERAL GRAINS THAT ARE NOT VISIBLY ALTERED
- C. WHEN COMPARING LIKE MINERALS IN THE SAME SLIDE, THE VARIATIONS OF A ABOVE ARE NOT RESPONSIVE TO:
 1. PROXIMITY OF ANALYZED SPOT TO GRAIN EDGE
 2. SHIELDING OF GRAIN BY INCLUSION IN LARGE HOST MINERAL
 3. PROXIMITY OF ALTERED AREA IN SLIDE
- D. ZONING OCCURS BUT THERE ARE NO TRENDS IN ZONING BETWEEN LIKE MINERAL GRAINS OR BETWEEN DIFFERENT MINERAL TYPES IN THE SAME SLIDE
- E. VARIATIONS IN ABUNDANCE OF OTHER ELEMENTS IN THE MINERALS DOES NOT INDUCE VARIATION IN ABUNDANCE OF EITHER HALOGEN OR THE WATER IN THE MINERAL
- F. WHEN COMPARING LIKE MINERAL GRAINS FROM THE SAME STOCK, THE VARIATIONS ARE NOT RESPONSIVE TO VARIATIONS OF:
 1. MODAL COMPOSITION OR TEXTURE OF SAMPLES WITH LIKE WHOLE ROCK CHEMISTRY
 2. VARIATIONS IN DEGREE OF ALTERATION
 HOWEVER, THEY ARE RESPONSIVE TO VARIATIONS IN:
 3. ROCK CHEMISTRY
 4. SAMPLE AGE

Figure 8.

(1) the variations are not responsive to factors that would have shielded the grains or analytical spot from access to an aqueous phase, and (2) although zoned, the grains do not show trends in their zoning patterns. In addition, the variations are not the result of coupled substitution with other elements in the crystal lattice (fig. 8E) or processes that changed texture in the rock or even caused incipient alteration in the rock (fig. 8, F1 and F2). However (fig. 8, F3 and F4), they were influenced by changes in the magma, but only measurably by those that involve long-term changes, such as differentiation and decrease in age. These trends are illustrated in figures 9 through 11.

The top of figure 9 indicates a negative correlation of chlorine abundance in apatite with differentiation index of the igneous series as a whole, and also for the Rattler Granodiorite alone. A slight negative trend is perhaps possible for the chlorine content of biotite, but the chlorine content of hornblende, which is near the limit of detection, indicates no apparent trend with change in rock chemistry. However, note that the apatite and biotite in the Granite Mountain Porphyry contain much less chlorine than apatite and biotite in the older rocks.

A positive correlation between the differentiation index and the fluorine contents of biotite and apatite are shown in figure 10; also indicated is that the minerals from the younger rocks contain more fluorine than those in older rocks. The thrown points from the trends (the filled circles) are from dike samples that are more likely subject to gain or loss of Cl, F, and H₂O than samples from the stocks. Again, hornblende shows no trend, but igneous sphene, which was analyzed after the figure was drafted, demonstrates even stronger correlations than those shown by biotite and apatite. Figure 11 shows the H₂O content of the minerals derived by calculation; these correlations are not strong but are consistent, for the H₂O content of both biotite and apatite correlate negatively with differentiation of the rocks, as does the calculated H₂O content of sphene, not shown in the figure (Banks, 1976).

In summary, Cl and H₂O contents of the minerals decrease or show no trend with differentiation and decreasing age of the samples while their F contents increase. Importantly, comparison of these trends with those published for other calc-alkaline stocks and igneous series elsewhere in the world demonstrates that the Ray data are not unique (Banks, 1976).

One of the objectives of the study was to determine the contents of the halogens and water in the whole-rock samples. This was done using modal data (fig. 12), measured specific gravities, and the mineral analyses. These calculated values represent the amount of Cl, F, and H₂O that was present in each rock sample immediately after its final consolidation and degassing, if any, and eliminated problems of

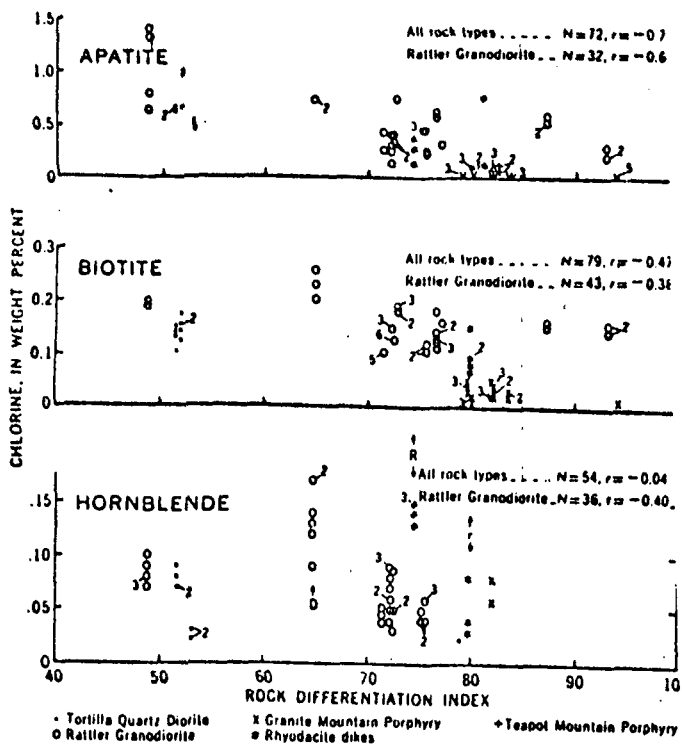


FIGURE 9.—Variations of Cl content of mineral with rock differentiation index (from Banks, 1976)

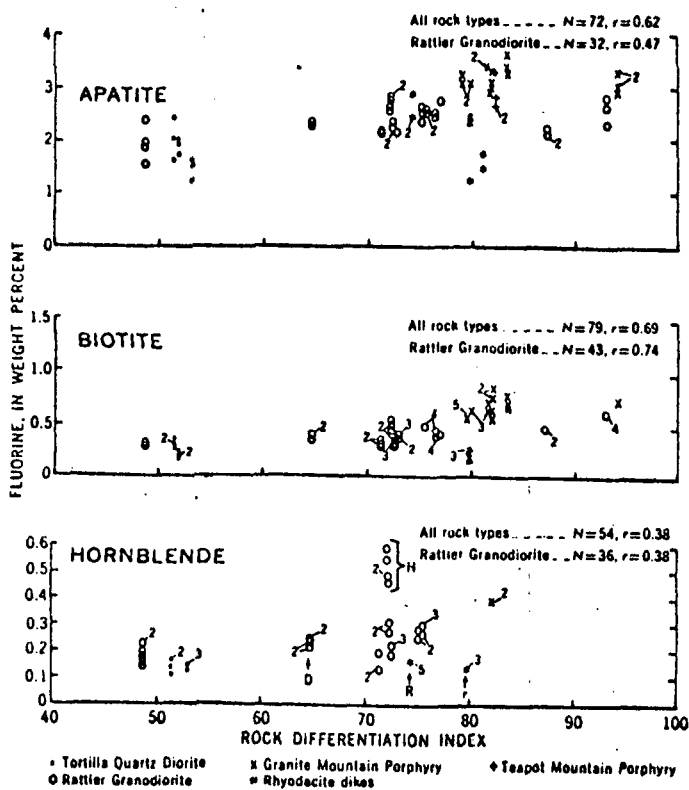


FIGURE 10.—Variations of F content of mineral with rock differentiation index (from Banks, 1976)

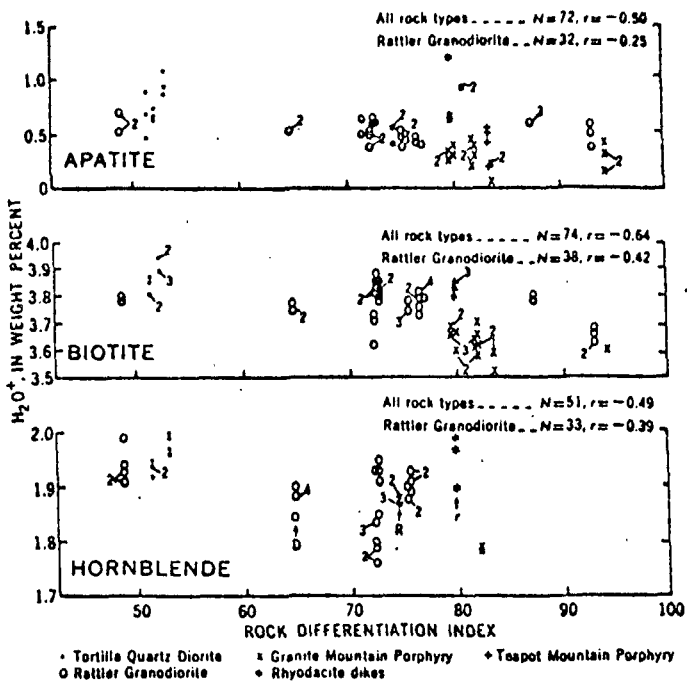


FIGURE 11.—Variations of calculated H₂O⁺ content of mineral with rock differentiation index (from Banks, 1976)

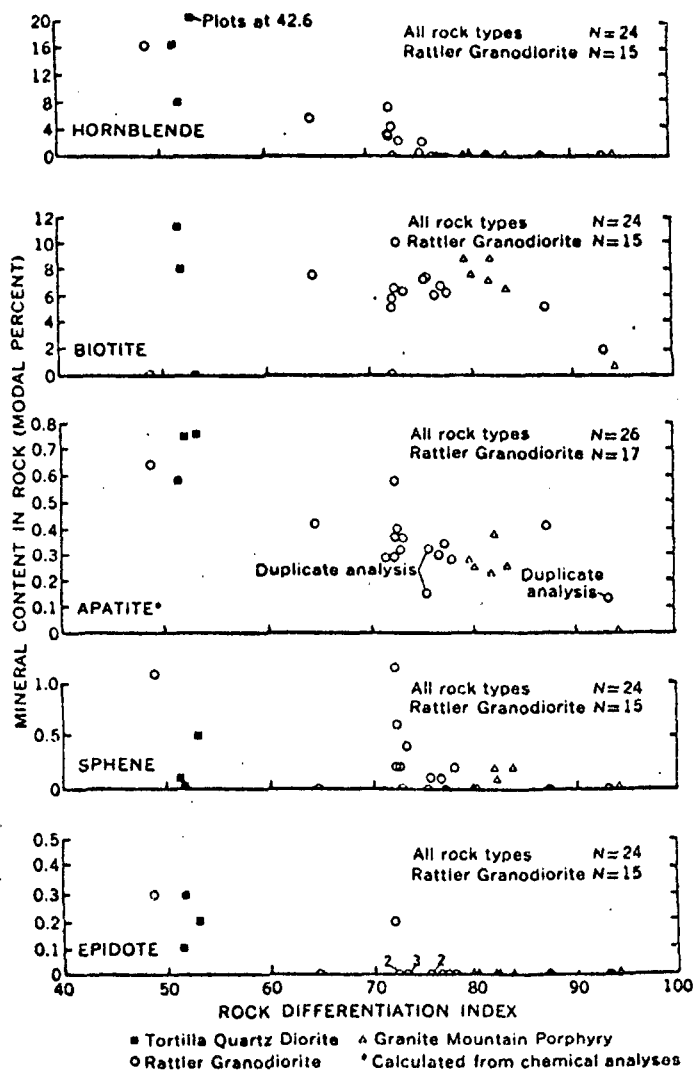


FIGURE 12.—Variation of mineral modal abundance with rock differentiation index (from Banks, 1976)

loss or gain of ore-fluid components caused by incipient alteration. Calculated H₂O contents of the samples show a decrease with differentiation of the igneous series (fig. 13C; 13A and 13B are not discussed but deal with alteration phenomena). A similar decrease in Cl content of the samples is observed in figure 14A, but because of the opposing trends of increases in the mineral content of F (fig. 10) and decrease in modal abundance of hydrous minerals (fig. 12), no pattern develops for F except perhaps a drop of its content in the aplites. No correlations were found between the rock texture or modal ratio of mafic minerals in the rocks and the calculated Cl, F, or H₂O contents of the samples.

Cl and F contents by analysis of the rocks are also shown in figure 14 (the horizontal arrows). Note that the trends for the measured values agree with the calculated ones, but that in all but one case, these arrows indicate lower contents than the corresponding calculated values. This was expected for Cl because the secondary hydrous phases contain less Cl than is present in the igneous hydrous minerals (fig. 2) and all the rocks have experienced incipient alteration of the primary phases. Again, and importantly, the trends in figures 13 and 14 are the same as those for comparable data in the literature from other calc-alkaline stocks and igneous series (Banks, 1976).

In brief summary, although variations in abundance occur in the halogen and water contents of the minerals, they do not respond to any igneous or secondary geologic parameters except the age and indicators of differentiation of the rock samples. Some of the minerals show trends of their Cl and H₂O contents less and their F contents higher in younger more silicic samples. Calculated halogen and water contents of the unaltered rock indicate trends like those of the minerals, except for the F content of the rocks, for which there is no change with differentiation except perhaps a decrease in abundance in the most differentiated aplites. Finally, the trends of changes of abundances of halogens and water for both the rocks and minerals are the same for the Rattler Granodiorite as for the entire igneous series, and also for the data and trends for comparable calc-alkaline plutons and igneous series elsewhere in the world, even those not associated with ore or ore-forming provinces. This last statement adds still another set of conditions for the orthomagmatic model because even with respect to the H₂O and Cl components of ore fluids, the rocks and minerals that should have monitored the development of an ore fluid at Ray did not record anything unique. And, in fact, they were monitoring for all practical purposes what appears to be a decrease in the activities of Cl and H₂O rather than an increase.

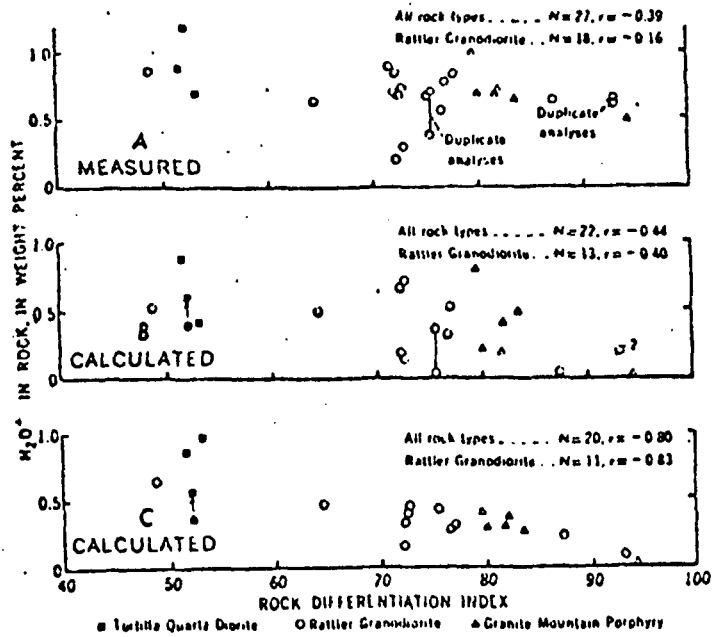


FIGURE 13 —Variation of H_2O^+ contents of rock sample with rock differentiation index. A, Measured. B, Corrects A by removing effects of alteration products. C, Calculated from rock and mineral densities, mineral analyses, and modal abundance of originally unaltered igneous minerals (from Banks, 1976).

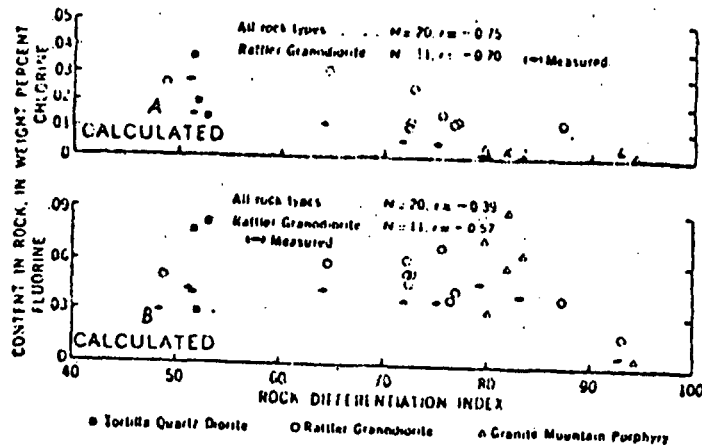


FIGURE 14.—Variation of Cl and F contents of rock samples with differentiation index. Symbols represent calculated values; arrows represent measured amount in water-leached rock powders (from Banks, 1976)

As in the interpretation of most geologic data, there is more than one explanation possible of those for the Ray rocks. However, unless one postulates that the Ray plutons are not related to the one hypothesized to have formed the deposit, the alternatives available either do not favor an orthomagmatic model for Ray or they require some rather questionable new special conditions for it to survive (Banks, 1976). The explanation that best fits the data is that the magmas were all undersaturated when emplaced; saturation was averted by separation of the hydrous minerals from the melts, separation of those minerals depleted the melts of Cl with respect to the much more soluble F, and the increase in F content of the minerals resulted from a decreasing number of hydroxyl minerals forming in the melt in which the residually concentrated F could be accommodated. Thus, very little water evolved from the magmas and its access to the Cl in the system was very restricted. The millimeter-scale variations in the abundance of the Cl, F, and H₂O, I attribute to local millimeter-scale or less, supply and demand.

The apparent lack of evolution of vapor from the magmas is consistent with increase in the F content of biotite with development of the individual plutons and igneous series as a whole, because given the expected decrease in temperature of the younger magmas and the stable or decreasing oxygen fugacity suggested by the slight decrease in Mg content of biotite, biotite in the older melt should have incorporated more rather than less F compared to biotite in the younger melts (see fig. 10), had much vapor been escaping the melts. Moreover, hydroxyl-fluorine exchange between biotite and water is rapid at magmatic temperatures, thus the measurably different F contents of biotite in the same sample argue against the presence of much magmatic vapor phase.

So far I have only discussed data that apply to the first four conditions of the orthomagmatic model (fig. 5), which from the standpoint of a chemist and geologist are equally as important as the last condition. However, it is the last one that holds fascination for the stockholder and miner of deposits, for without copper or sulfur there would be no deposit. So we will move on to the second part, the magmatic sulfide minerals in the rocks, their modal and textural relationships, and how petrologic interpretation of them relates to condition five (fig. 5), the magmatic behavior of copper and sulfur.

The magmatic sulfide minerals are pyrite, chalcopyrite, bornite, and possibly covellite. They are small (fig. 15), averaging about 30 square micrometers, in area, or about 6 microns across, although a few have diameters up to 70 microns and are as much as 4,000 square micrometers in area. One of the features which suggests that they are magmatic is that they occur enclosed and often around the cores of other magmatic minerals, without benefit of fractures or alteration. Other features indicate, in addition, that they separated at least in

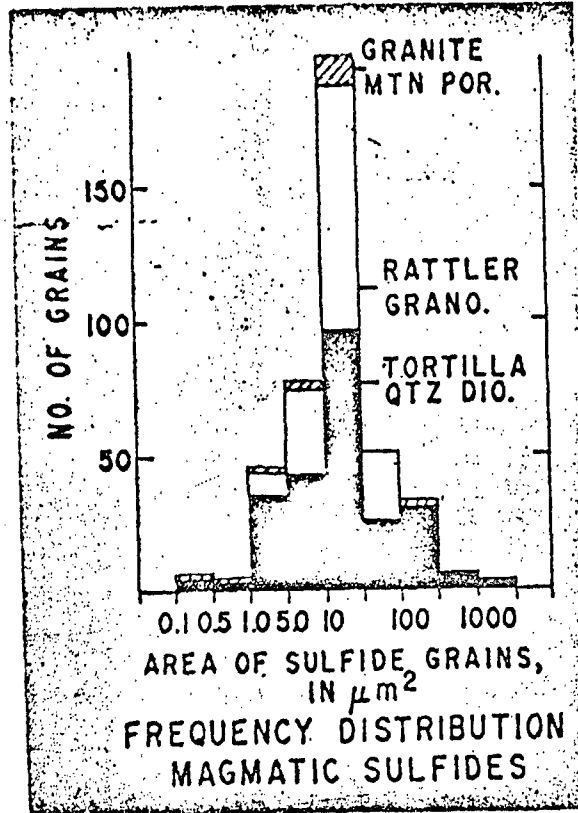


Figure 15.-- Size distribution of individual magmatic sulfide grains in Laramide rocks associated with the Ray porphyry copper deposit.

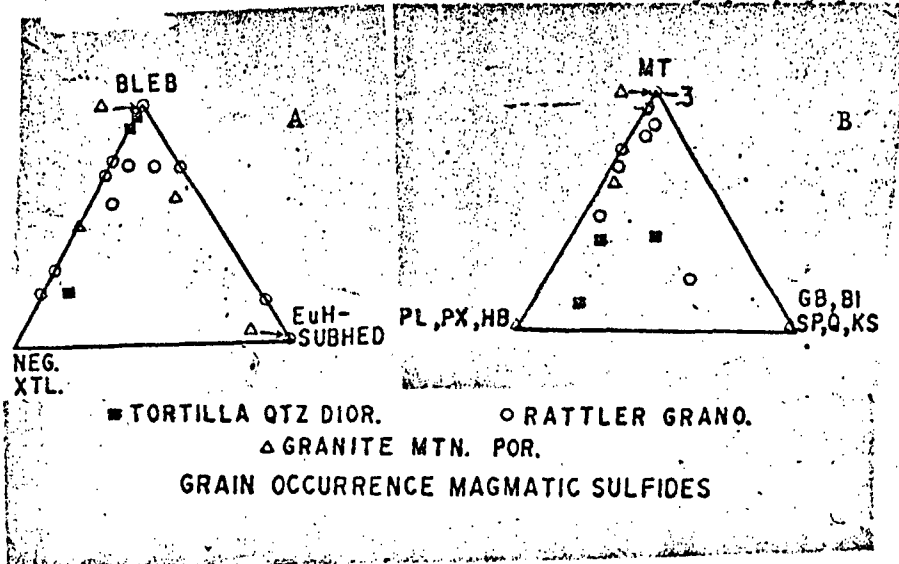


Figure 16.-- Grain form (A) and host mineral occurrence (B) of magmatic sulfide grains in Laramide igneous rocks near the Ray porphyry copper deposit, Arizona (Neg. xtl. = negative crystal; euh-subhed = euhedral and subhedral; MT = magnetite host mineral; PL = plagioclase host mineral; PX = pyroxene host mineral; HB = hornblende host mineral; GB = grain boundary occurrence; Bi = biotite host mineral; SP = sphene host mineral; Q = quartz host mineral; KS = potassium feldspar host mineral.

part as immiscible liquids. These features are that most are bleb shaped or fill negative crystals in other magmatic minerals (fig. 16A) and, that many are two phase. Still other features are that their mode of occurrence, the host mineral most frequented (fig. 16B) and their size, modal abundance, and pyrite to copper ratios change systematically with change in host-rock age and composition. Some of these relationships are illustrated in figures 17-21.

In figure 17A and B, the locations of sulfide minerals are in the small outlined areas in the cores of pyroxene twins and pyroxene grains. This is a common location for the occurrence of the sulfides in the more mafic samples. In figure 17C, the sulfide grains located in figure 17A, are seen to be two-phase chalcopyrite-bornite, and in figure 17D, the grain is two-phase chalcopyrite-pyrite. Although the grains in both examples have some linear edges, the edges are parallel to crystallographic planes of the host pyroxene, and because they are two phase, the common linear edge cannot represent the crystallographic edge of either sulfide mineral. This suggests that the sulfide grains represent immiscible liquids and that they fill negative crystals in the host pyroxene. Another common site for sulfide grains is the core of plagioclase, as seen in figure 18A. Figure 18B is an enlargement of the core area of figure 18A, and shows chalcopyrite filling negative plagioclase crystals, some of which are elongate parallel to the [010] face of the host mineral and some of which are enlarged in steps along [100] faces of the plagioclase host to more blocky grains. In all rock types, it is magnetite that is the dominant host mineral of the sulfide minerals (fig. 16B, fig. 19). In figure 19A, two-phase pyrite-chalcopyrite blebs occur with several different silicate phases in negative crystals of the magnetite. Note that the sides of the multiphase negative crystals parallel the external faces of the magnetite grain and that conversion of the magnetite to hematite, part of it on fractures, is not accompanied by corrosion of the sulfide grains. Another chalcopyrite bleb plus silicate in a tabular negative crystal in magnetite is illustrated in figure 19B.

Figure 16B summarizes the foregoing, or that sulfide grains in the more mafic samples, indicated by the three Tortilla Quartz Diorite samples and the mafic Rattler Granodiorite sample, occur with some frequency in the early-formed silicates, and to some extent with the interstitial silicate minerals, but that the dominant host is magnetite. In the more differentiated samples, magnetite is commonly the sole host mineral (fig. 16B).

The response of the sulfide minerals to chemistry of the host rock, a decrease in size and modal abundance of the sulfides in progressively younger and more differentiated samples, is shown in figure 20. The copper sulfide to pyrite ratio of the grains in the sample is not shown in the slide, but it also decreases in the younger, progressively more differentiated samples. Again, these findings are not unique compared

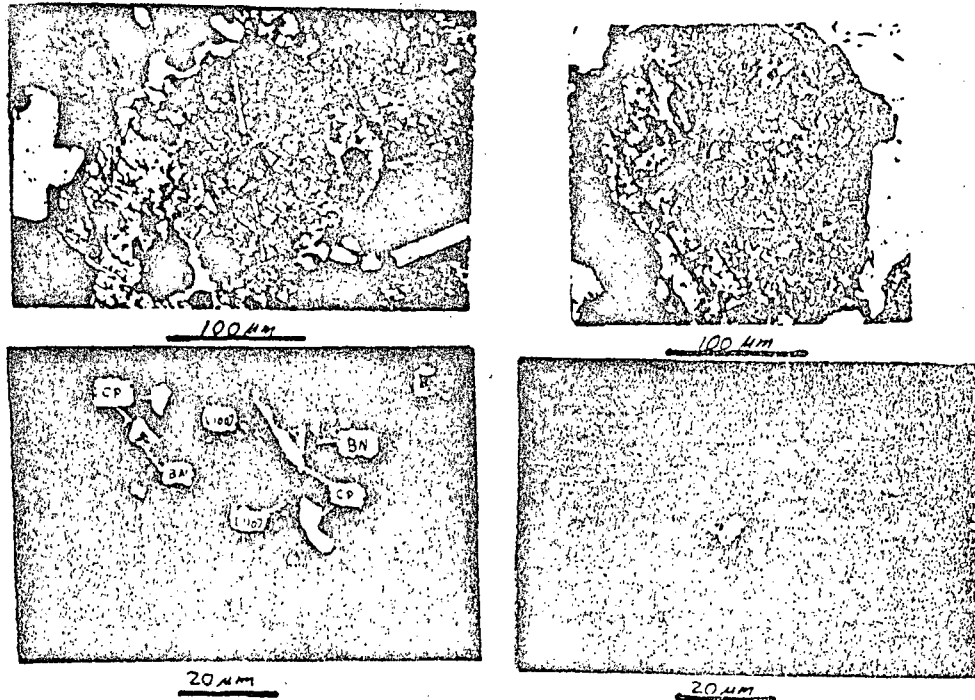
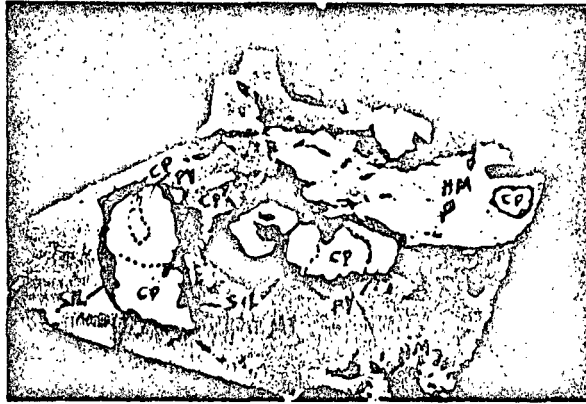


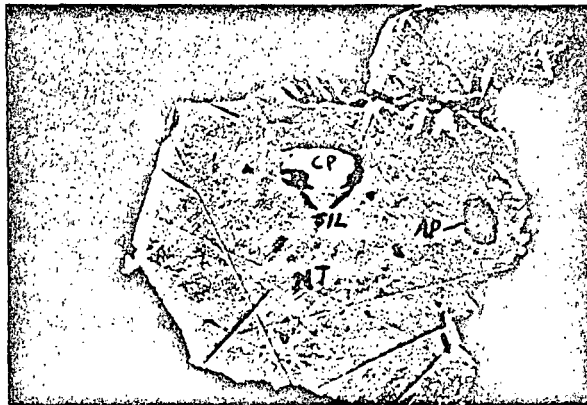
Figure 17.-- A and B., Occurrences of sulfide grains in cores of pyroxene grains, Tortilla Quartz Diorite; C., Enlargement of area shown in A., dotted lines show [100] and [110] cleavage of host pyroxene surrounding the two-phase chalcopyrite-bornite grains; D., Enlargement of area shown in B., dotted lines show [100] cleavage of host pyroxene surrounding the two-phase chalcopyrite-pyrite grain in pyroxene negative crystal. (PX = pyroxene, HB = hornblende, CP = chalcopyrite, BN = bornite, PY = pyrite).



Figure 18.-- A. Chalcopyrite filling negative crystals around optical core of plagioclase grain, partially crossed nicols; B. Enlargement of core area of plagioclase, uncrossed nicols, CP = chalcopyrite, MT = magnetite, PL = plagioclase.



100 μ m



20 μ m

Figure 19.-- A. Two-phase chalcopyrite-pyrite grains and silicate phases filling negative crystals in magnetite, reflected light. Hematite, probably of postmagmatic origin replaces part of the magnetite; B. Chalcopyrite bleb and silicate filling negative crystal in magnetite, reflected light. (MT = magnetite, HM = hematite, CP = chalcopyrite, PY = pyrite, SIL = silicate phases, AP = apatite.

to other rock sequences. Thus, even with respect to the sulfide minerals in the magma, the Ray rocks are not unique, compared to igneous series not related to porphyry deposits.

The above-described textural relations, and their responses to change in primary petrologic parameters in the rocks, strongly support a magmatic origin for the sulfides. Furthermore, because they appear not to be influenced by proximity of incipient alteration in the slide (compare fig. 19A and B), or overall alteration of the samples (as indicated by the lack of response of their modal abundance to the degrees of alteration of either biotite or plagioclase in the sample, see fig. 21), the trends and textural data are reasonably interpreted to be commenting about processes that were occurring in the magmas.

A summary of the petrologic data and interpretations on the behavior of copper and sulfides in the magma is given from A through G of figure 22. A, the presence of the magmatic sulfides indicates that the melts were saturated at least locally with sulfides, but with modal abundances averaging 5 ppm, the saturation of sulfides occurred very infrequently. B and C, the textural data, when viewed in the light of recent experimental data, suggest that the sulfide saturation was not only infrequent, it probably was attained locally on a micron or millimeter scale, in response to local enrichment due to formation of other crystalline phases rather than to a general saturation of the melts. To expand, as shown earlier (fig. 16B), in contrast to the more differentiated samples, the sulfide minerals in the more mafic (older) samples occur in large part in and around the cores of pyroxene, hornblende, hornblende after pyroxene, and plagioclase. These occurrences can be explained by local enrichment and saturation of the sulfides in the cooling melt caused by rejection of sulfur from the early-formed sulfur-poor pyroxene and plagioclase. The relatively fewer occurrences of sulfide minerals in the later forming biotite, quartz, and potassium-feldspar, and outer rims of hornblende, pyroxene, and plagioclase, can be attributed to fewer occurrences of saturation of sulfides because these minerals and parts of minerals were forming when apatite, biotite, and hornblende were forming in the melt, and, as will be shown later, these hydrous minerals extracted sulfur from the melt. Presence of the sulfide grains interstitial to the last-formed silicates in the more mafic samples, can be explained by continued decrease of melt temperature and continued crystallization of the sulfur-poor silicates while a decreasing amount of biotite and apatite was precipitating from the melt. Finally, magnetite is the dominant host of the sulfide minerals in the majority of the samples, particularly the more felsic ones, in which magnetite is essentially the only host mineral. If, as suggested by extremely low modal abundance of the sulfide minerals, the melts were generally undersaturated with sulfides, their preference for magnetite is not surprising because sulfur saturation in silicate melts is strongly and directly dependent on its iron

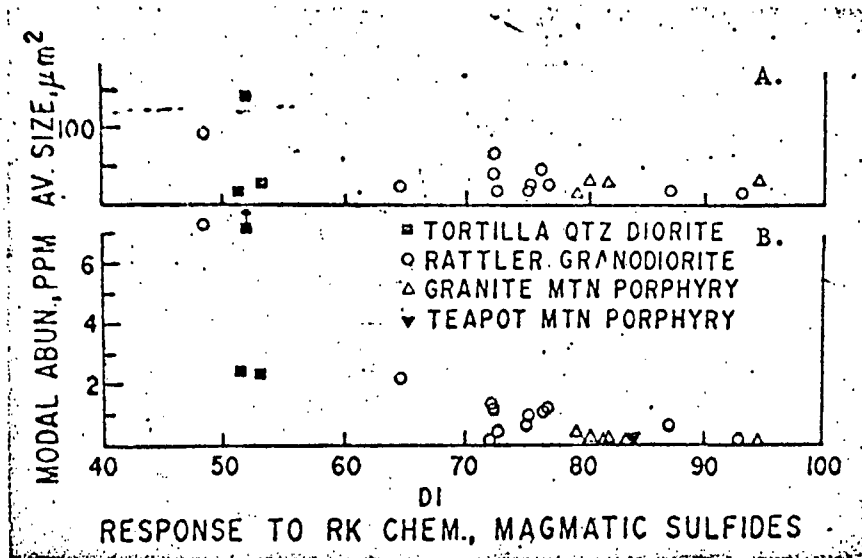


Figure 20.-- Variations of average size (A) and modal abundance (B) of magmatic sulfide grains with differentiation index of Laramide host rock near Ray, Arizona.

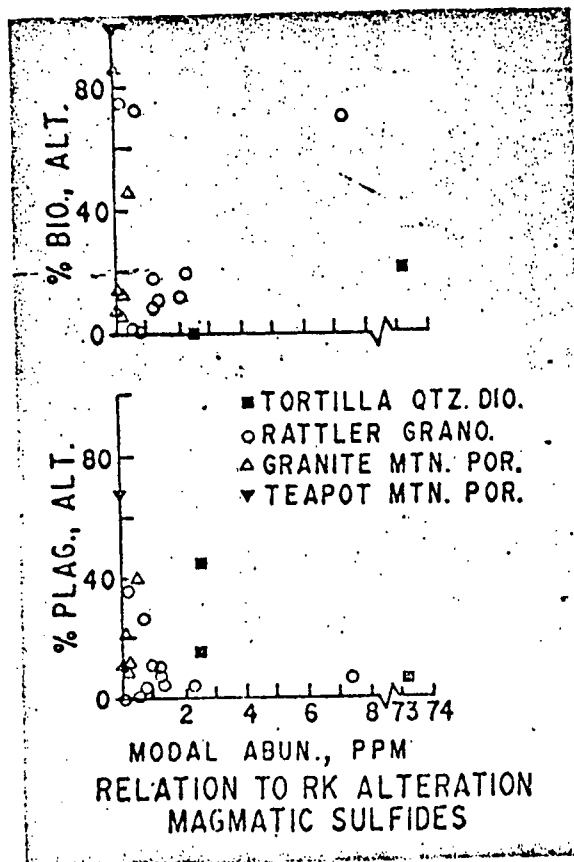


Figure 21.-- Relationship between alteration of biotite and plagioclase and modal abundance of magmatic sulfide grains in Laramide rocks near Ray, Arizona.

content. Thus, inducement of sulfide saturation caused by removal of iron from the melt by the growing magnetite, adequately explains its dominance as the host mineral for the sulfide minerals.

Three observations in the sulfide petrology data suggest that the younger melts had less initial sulfur than the older melts (fig. 22F). One is the decrease in sulfide grain size and abundance in the younger rocks compared to the older more mafic rocks (fig. 22D). The second (fig. 22E), indicates that these changes are not the result of secondary processes imposed on the samples. And third, the sulfide minerals formed later in the crystallization sequence of the younger magmas than in the older magmas. This last point is supportive of the decrease in sulfur content of the younger melts because (1) relative to the more mafic samples, more sulfur-poor silicates (plagioclase, potassium-feldspar, and quartz) formed in the felsic rocks prior to formation of the sulfur-bearing biotite and apatite, which in addition are less abundant in the more felsic samples than in the mafic samples; (2) the more differentiated magmas were probably emplaced at lower temperatures; and (3) if experimental data for basaltic melts can be applied to the Ray magmas, the sulfide-carrying capacity of the younger magmas should have been lower because of their more felsic chemistry. Finally, younger samples, required, in addition, precipitation of magnetite to induce sulfide saturation, while in the mafic samples magnetite separation helped but was not required.

The decrease in sulfide content of the rocks with differentiation of the samples does not favor the hypothesis that the sulfide grains were removed by a magmatic vapor phase (fig. 22G), and the textural and modal data are adequately explained in the framework of water under-saturated magmas, in agreement with the field and halogen-mineral data presented earlier. On the other hand, the sulfide petrologic data do not in themselves rule out evolution of water from the magmas. However, neither evidence that water of the required quantity did evolve nor quantification of whether it could have evolved are presently available. As examples, evolution of water from the magmas would have increased their oxygen fugacities and induced precipitation of magnetite and sulfide grains. Countering this tendency would be the increase in temperature of the magmas from heat of crystallization, the amount dependent on the amount of melt involved, amount of water evolved, and depth of emplacement. Countering this in turn, would be removal of heat from the magma during expansion and egress of the magmatic vapor phase, this amount also dependent on pressure changes and amounts of vapor and magma involved. Furthermore, removal of gaseous sulfur species in the water would have tended to avert sulfide precipitation, but as shown later, the sulfur content of other igneous phases forming in the magmas at the same time as the magnetite and sulfides did not record a measurable trend with differentiation of the stock or even when comparing minerals from samples with textures as different as granitoid and porphyritic, the latter texture commonly suggested to be the result of degassing of magma.

A final observation concerning the sulfide petrology is the decrease in copper sulfide to pyrite ratio with differentiation of the samples and the accompanying decrease of modal abundance of the sulfides. The former trend is expected because of the chalcophile tendency of copper, and both trends argue strongly for decreasing activity of copper in the melt as the stocks became younger.

In summary, the textural and modal data for the sulfides is simply and adequately explained (1) if the oldest stocks did not have much copper and were undersaturated in sulfide, and (2) if the progressively younger stocks were intruded with less of copper and sulfur, and (3) if saturation of sulfide in the melts was induced by very local millimeter-scale crystallization-equilibrium processes in the magmas. The data do not find easy accommodation with the hypothesis that much water evolved from the melts. None of these interpretations favor the five basic conditions that make the orthomagmatic model a viable model for the Ray deposit (fig. 5).

Still another possibility to explore is that copper and sulfur were removed from the melts, stored in other major mineral phases, and then supplied to a presumed last gaseous effluent of the magma. This third part of the report was investigated initially by electron-probe analyses for copper and sulfur of all the major and minor igneous minerals in the rocks. Part of these data, that for biotite, has already been published (Banks, 1973; 1974) and was discussed earlier. In brief, sulfur was found to be ubiquitous in biotite, and copper occurs below the 100 ppm detection level of the electron probe in all of the nonsulfide minerals in the rocks except for an occasional biotite grain, and this copper is very likely in chlorite or vermiculite and not related to the igneous history of the samples.

At about this time in the study the ion microprobe with the detection levels for copper as low as 1 ppm became available, and I was able to check the minerals again, this time at detection levels that were more appropriate to a hidden copper source in the rocks. However, the results of the ion-probe study indicate that plagioclase, potassium-feldspar, quartz, hornblende, and pyroxene contain essentially no copper, and that although copper occurs erratically in some biotite grains (between 1 and 40 ppm) and always in magnetite (also between 1 and 40 ppm), the combined contribution to the samples from these sources is less than 4 ppm. Furthermore, the highest copper values for magnetite occur, not without exception, in the samples with detectable copper in biotite, and these samples also have abundant copper-bearing secondary minerals after biotite. Thus the likelihood of a secondary origin of even this small amount of copper is at least likely. Moreover, there is no correlation between texture, differentiation, or age of the samples and the copper content of the biotite or magnetite. Thus, it has been demonstrated that (1) very little copper occurs in the rocks in sites other than magmatic sulfides, (2) there is strong suspicion that the little copper detected in other minerals may result

from secondary processes, and (3) no trends of copper enrichment occur in any magmatic mineral.

The study further discloses that enrichment of sulfur with differentiation of the igneous rock does not occur in the minerals that contain it (fig. 23). These minerals are biotite (average 200 ppm sulfur), apatite (average 700 ppm), and hornblende and igneous epidote (both with about 50 ppm S and not shown in fig. 23). As suggested by the scatter in the data (fig. 23), the abundance of sulfur in the minerals is measurably, often extremely, different in like mineral grains in the same rock type, same stock, same thin section, and even the same mineral grain. In addition, the sulfur abundances do not respond to changes in chemistry of the minerals, to proximity of the grain to alteration in the thin section, to inclusion or lack of inclusion of a grain in another mineral, to overall alteration in the sample (fig. 24), to proximity of the analyzed spot to the grain edge (fig. 25), or to rock texture (fig. 26). These factors indicate that, like the Cl-F data for the same minerals, the sulfur contents vary measurably and are not detectably related to exchange with an aqueous phase, but, in contrast to the Cl-F data, the variations in sulfur abundance also are not responsive to any measurable change in the magmas. However, this is not inconsistent with the explanation of the Cl-F data or the sulfide petrology, because all are compatible with an interpretation that the variations in contents of the trace elements in the minerals resulted from local processes of supply and demand occurring over millimeter or less distances in the melts. Thus, whole-rock petrologic parameters such as texture and a differentiation index are too gross to permit definition of the conditions that induced variations in abundance of sulfur in the minerals.

Finally, what are the likely copper and sulfur contents of the magmas? If, as seems likely from the wide variety of data for the rocks, little sulfur or copper was removed from the rocks or minerals at the magmatic stage, then the copper and sulfur contents of the rocks calculated from the mineral analyses indicate their contents in the magmas. Thus, the calculated maximum copper content of the samples (see fig. 27B), indicates a low copper content, on the order of 10-20 ppm, for the magmas that were associated with Ray. Comparison with the measured copper content of the samples (fig. 27A), indicates that the whole rock samples have been enriched some 10 or more times in copper by the alteration minerals, chlorite and vermiculite. The lack of trend in the calculated copper content of the rocks with their differentiation index, results from use in the calculation of the detection limit for copper for the major silicate phases on the rocks, which although small, swamps out the negative correlation that occurs when just plotting copper contributed to the samples from the magmatic sulfides. Calculated sulfur contents of the samples are also low, on the order of 20-30 ppm, and these values correlate negatively with increasing differentiation of the samples, a trend expected because of the decrease

SUMMARY OF SULFIDE PETROLOGIC DATA AND INTERPRETATIONS

- A. IMMISCIBLE SULFIDE MELT FORMED IN THE RAY MAGMAS BUT NOT MUCH, 5 PPM, MAX 75 PPM
- B. SULFIDES FOUND IN SPECIFIC LOCATIONS AND ONLY A FEW OF THOSE POSSIBLE, SUGGESTING THAT LOCAL CONTROLS INDUCED SULFUR SATURATION
- C. PREFERRED GRAIN LOCATIONS EXPLAINABLE BY EXPERIMENTAL DATA IF SULFUR SATURATION WAS LOCAL
- D. SULFIDE SIZE, ABUNDANCE, AND COPPER-SULFIDE/IRON-SULFIDE DECREASE WITH DIFFERENTIATION AND YOUNGING OF HOST ROCK
- E. SULFIDE ABUNDANCE NOT RESPONSIVE TO ALTERATION OF HOST ROCK OR TO INCIPIENT ALTERATION IN SLIDE
- F. MODAL AND TEXTURAL DATA SUGGEST YOUNGER MELTS HAD LESS INITIAL SULFUR THAN OLDER MELTS
- G. MODAL AND TEXTURAL DATA DO NOT FAVOR GENERAL SATURATION OF THE MELTS WITH SULFUR OR EVOLUTION OF WATER FROM THE MELTS

Figure 22.

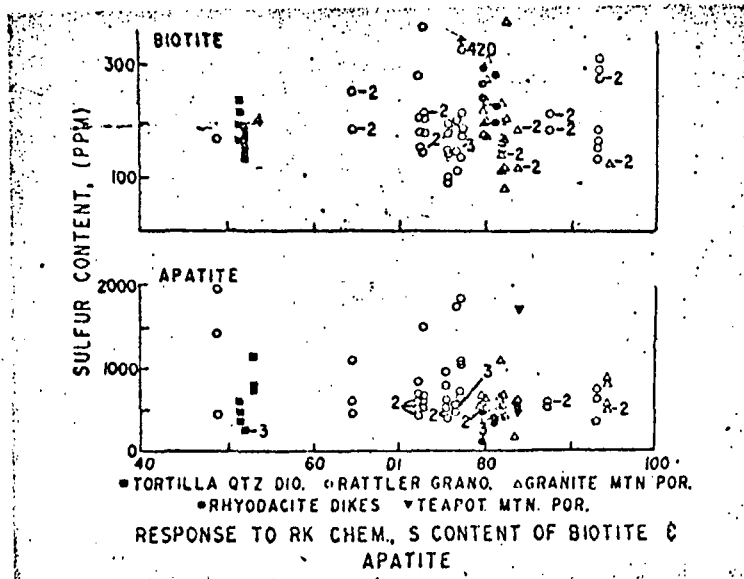


Figure 23.-- Variations of sulfur content of biotite and apatite with rock differentiation index.

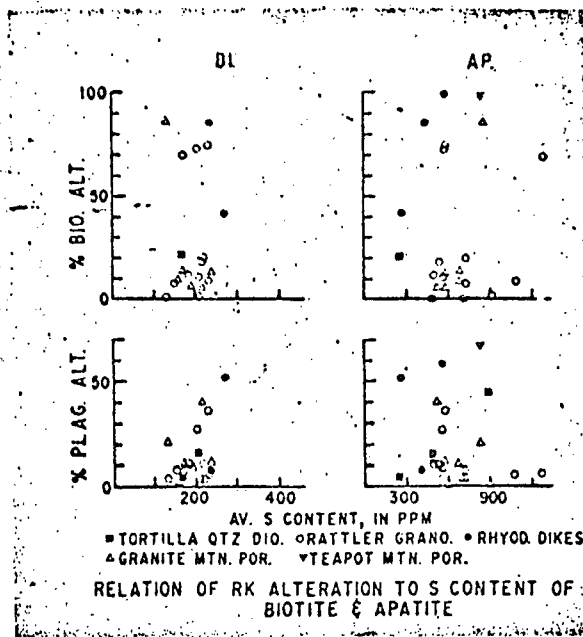


Figure 24.-- Relationships between average sulfur content in biotite and apatite and the percentage of biotite and plagioclase altered in the rock, Laramide igneous rocks near Ray, Arizona.

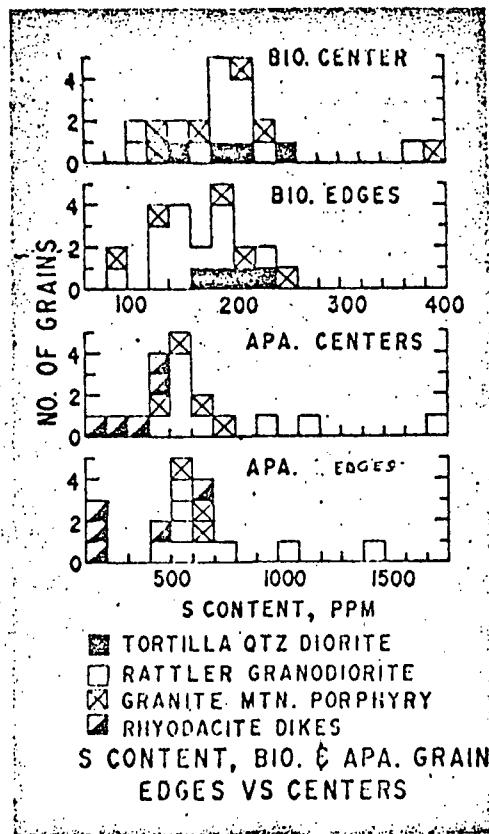


Figure 25.-- Frequency distribution of sulfur contents in the centers and edges of igneous biotite and apatite, Laramide igneous rocks near Ray, Arizona.

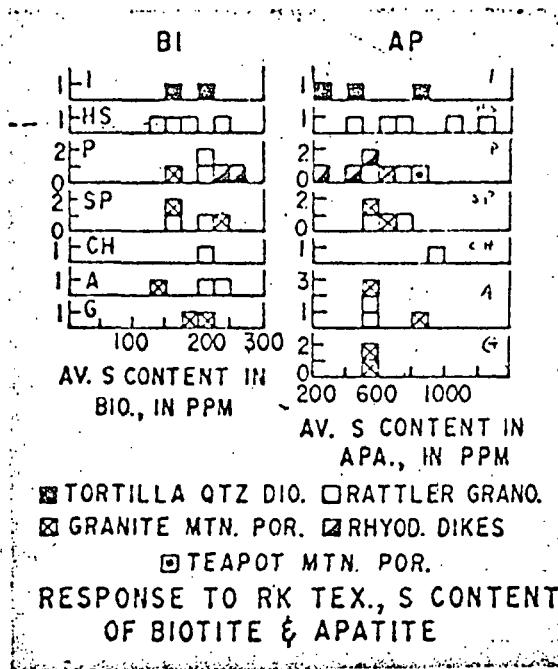


Figure 26.-- Frequency distribution of the average abundance of sulfur in biotite and apatite in samples with differing textures (AP = apatite, BI = biotite, I = intersertal texture, HS = hypidiomorphic seriate texture, P = porphyritic texture, SP = seriate porphyritic texture, CH = chilled border phase, A = aplitic dikes, G = granitoid texture).

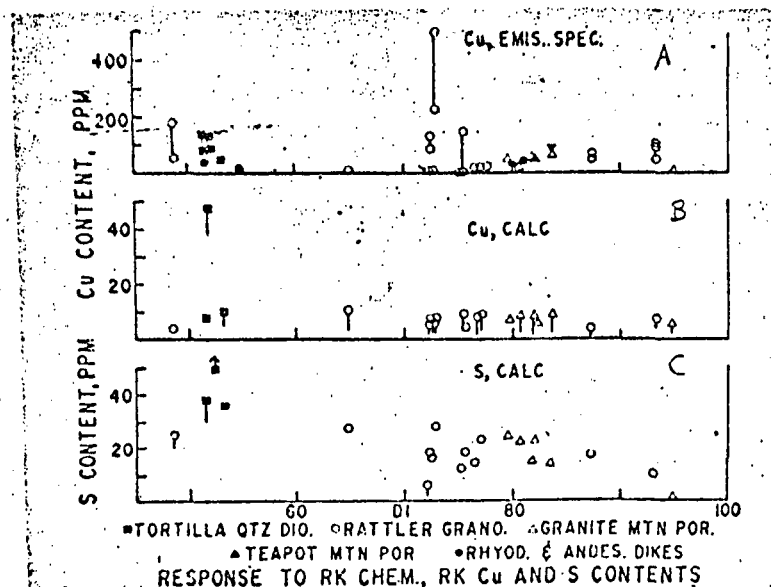


Figure 27.-- Variation of copper and sulfur contents of Laramide rocks near Ray, Arizona, with differentiation index. A. Copper content measured by emission spectroscopy. B. Probable maximum copper content of samples calculated from mineral analyses and modal abundances. C. Probable sulfur content of samples calculated from mineral analyses and modal abundances. Tails on symbols in B. and C. point to calculated values assuming 0 ppm rather than the detection limit of the analytical instrument for the minerals with undetected copper and sulfur.

in abundance of both the sulfide and hydrous minerals with differentiation (figs. 20 and 12).

Thus, direct measurement of the minerals that should have monitored the development of the major components of an ore fluid in any parental batholith of the Ray igneous suite show trends that are not supportive of the orthomagmatic model. In addition, when interpreted in the simplest petrologic manner that is compatible both with field and petrologic data for the rocks and with applicable experimental systems, the Ray stocks, and by analogy the parent batholith if any, were unlikely to have produced much aqueous fluid and the best sources of Cl, S, and Cu in the melts were unlikely to be physically very available to the small amount of fluid released. Neither does the data directly from the rocks favor the meteoric water model. Furthermore, the data for the Ray rocks and minerals are not unique when compared with comparable data from rocks in other porphyry environments or even those in barren geologic provinces. Therefore, it seems appropriate, as well as economically expedient, to evaluate what the very real space-time relationship between porphyry deposits and associated plutons really means, and to do that evaluation in the light of the data provided for the magmas at Ray. One such attempt has been released recently (Banks and Page, 1977). It is a model whereby the insolubility of sulfur in the felsic melts causes sulfide minerals to accumulate near but not in the magmas at the zone of partial melting that produced the Ray stocks. These sulfide accumulations are postulated to have been remobilized from the zone of partial melting by water produced in or below the zone late in the history of magmatism in Arizona. Such an origin is believed consistent with petrologic observations of the Laramide rocks at Ray and probably elsewhere.

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