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J. E. K.

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Memo To: Porphyry Copper Discussion Group

Subject: 1971-72 Meetings

As most of you know, a group with the name above consisting of Tucson geologists with a "guts" interest in the geology and genesis of porphyry ore deposits met a half a dozen or so times last year. The meetings were interesting and fruitful for those attending. We would like to see the Group continue this year. It is planned to meet on the second Monday of each month, thus on next Monday, October 11, on November 8, and on December 13. The best meetings last year were those with the best attendance. If you are really interested in participating, please bend every effort to be at my home (740 W. Las Lomitas) next Monday at 8:00 til 10:00 p.m. for an organization meeting and (probably) to continue discussion of alteration mineralogy and its significance in sulfide-silicate environments. If you can then figure on that 'second Monday' as a regular event in your schedule, everyone involved will benefit.

See you soon!



John M. Gilbert
Associate Professor of Geology

JMG:srg

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JEK

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

SOME OBSERVATIONS THAT BEAR ON THE ORIGIN OF
PORPHYRY COPPER DEPOSITS

By Norman G. Banks and Norman J Page,
U.S. Geological Survey

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SOME OBSERVATIONS THAT BEAR ON THE ORIGIN OF PORPHYRY COPPER DEPOSITS

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ABSTRACT

Observations at Ray, Ariz., suggest that upper crustal calc-alkaline plutons associated in time and space with the deposit might not have been capable of producing much water by differentiation and that any water released likely had restricted access to the best copper-sulfur sources in the magmas. Observation of concentrations of sulfides around isolated pockets of partially melted rocks below the Stillwater Complex, Mont., suggest to us a variant model of porphyry copper generation that does not require calc-alkaline plutons to be the vessels that transport copper and sulfur to upper crustal sites.

ACKNOWLEDGMENTS

The objective of this paper is to suggest an alternative or variant model of porphyry copper generation. It is not intended to include, nor do we claim, rigorous citing of all work that led to development of the several concepts shared by our model and others. However, we have attempted in the text to point out where one or more of the several concepts in the model are shared by other recent workers. This citing, however, does not necessarily point to the originator of a given concept. The manuscript was greatly improved by the helpful comments of T. G. Theodore, G. K. Czamanske, H. T. Morris, R. O. Fournier, and G. W. Walker.

INTRODUCTION

The genesis of porphyry copper deposits remains a debated topic despite the large volume of literature devoted to it. Observations on the contents of Cu, S, H₂O, Cl, and F in rocks and minerals in the intrusive suite associated in space and time with the early Tertiary (Laramide) Ray porphyry copper deposit, Arizona, and characteristics of partly melted rocks, particularly in the country rocks below the Precambrian Stillwater Complex, Mont., suggest a variant model of porphyry copper generation that, to our knowledge, has yet to be published and that, in our belief, best fits existing knowledge and data on porphyry copper deposits. In our model, copper, sulfur, and base metals are carried by water attracted to sites of partial melting in the lower crust or upper mantle and, as the carrier water enters the melt, are concentrated around the melts. Later cooling of the melts in the zone of melting results (along with water furnished by meta-

morphic dehydration at deeper levels) in the fluids that leach and transport the concentrated copper and sulfur to porphyry-type environments. As acknowledged above, parts of this two-stage model are similar to previously published models, and it therefore incorporates the ideas and observations of others. Our model differs from the others in that we propose a mechanism for the concentration of copper and sulfur near but not in magma at sites of partial melting prior to their transport by water to upper crustal sites. The exposed and hidden upper crustal plutonic rocks near porphyry copper deposits are therefore considered to be associates of ore fluids rather than their parents.

OBSERVATIONS

Other models.--The field evidence indicating temporal and spatial relations between intermediate calc-alkaline igneous rocks and "disseminated" porphyry copper deposits is well documented and has led to assumptions of genetic ties between the igneous rocks and the deposits. These ties have been interpreted mainly as causal, and although many variants and combinations exist, the most popular models used to explain these assumed causal ties can be separated roughly into two end members. One is the "classical magmatic model" which maintains that the calc-alkaline magmas were the vessels that transported the metals, fluids, and sulfur from a deeper source to or near to the deposits. The second end member model, the "meteoric water model," postulates that the copper and sulfur were leached, transported and deposited during circulation of fluids of nonmagmatic origin, with the magma providing heat and perhaps some other components. A third model, not as popular as the others, assumes no causal ties between the calc-alkaline magmas and the deposits. It is a one-stage model in which water that is generated in the lower crust or in the mantle leaches and transports copper and sulfur to the porphyry environment. This third model is very similar to ours, particularly as described by Noble (1970, 1974). However, the previously published models do not include descriptions of the processes whereby the sources of carrier fluid and concentrated ore components are juxtaposed at depth.

We do not set out here to disprove or revoke any of these or other models. We do, however, conclude that although published suggestive data exist for each of them, unambiguous data are not yet published that *prove* them. For example, the postulated causal relationship between a nearby pluton and a deposit is based only on circumstantial time and space juxtaposition. Furthermore, experimental studies only indicate that under special conditions a melt might bear the amounts of Cl and H₂O (but not S and no data for Cu) required for a deposit, but nowhere has it been demonstrated that they *do* or that Cu, S, Cl, and H₂O behaved during differentiation of an implied source stock or batholith in the manner required by the "classical magmatic model." In fact, data for these components in the Ray intrusive rocks do not easily fit into this model without unsupportable speculation. With respect to the "meteoric water model," recent studies of stable

isotopes of alteration minerals do not prove that the deposits evolved by simple redistribution of wallrock and magmatic Cu and S through the medium of a meteoric water in a circulation system induced by magmatic heat. They require only involvement of meteoric water in the fluids that formed porphyry copper deposits. The "meteoric water model" also does not explain why silicic calc-alkaline plutons are favored above others to make ore-bearing circulatory systems (for example, gabbroic bodies are better sources of both heat and metals compared to quartz monzonite bodies). In addition, both the classical magmatic model and the meteoric water model have problems in explaining deposits where plutons of the appropriate age are missing, and when they are present, why one certain pluton of many emplaced in the same structural environment at about the same time was favored over the others to make ore. Finally, we consider to be formidable the logistics required for a one-stage model in which Cu and S are leached by water from a large low-grademantle-depth source rock and transported to and up a structural conduit to upper crustal sites without concentration of the fluid-born components. Therefore, lacking, in our opinion, proof or even strongly supportive observational data, we feel that the literature can support still another model of porphyry copper generation, one based on observational data, with some interpretations and speculations, on the intrusive rocks near the Ray porphyry copper deposit, Arizona, and partly melted rocks near the Stillwater Complex, Mont.

Ray, Arizona.—The Ray deposit, located approximately 120 km north of Tucson, Ariz., has many of the characteristics of a "typical" porphyry copper deposit (Lowell and Guilbert, 1970, p. 404). It differs somewhat from the "typical" porphyry copper deposit in that its center, although containing a small volume of ore-vintage igneous rocks, is located several kilometers east of the largest exposed mass of approximately ore-age calc-alkaline rock. This relation, however, is useful because the igneous rocks related in time and space with the deposit remain fresh enough for their original character to be investigated. At least 12 intrusive rock types of Laramide age occur in and near the Ray deposit (Cornwall and others, 1971; Banks and others, 1972). The igneous activity began in the area about 70 m.y. ago and continued for about 10 m.y. Ore deposition occurred about 60 m.y. ago (Banks and Stuckless, 1973). At least 11 of the igneous rock types are cut by sulfide veinlets, although not all crosscutting relations occur within commercial ore bodies.

The intrusive rocks are similar in composition, sequence of intrusion, and appearance to other calc-alkaline rocks throughout the world and around other Arizona deposits. Additionally at Ray: (1) the volume of aplite dikes cutting stocks is generally low, (2) pegmatitic dikes are rare, (3) thermal aureoles around both stocks and dikes are restricted and in some carbonate terranes are absent, (4) miarolitic features have not been identified in field exposures or thin sections of the Laramide stocks, and (5) fluid inclusions in quartz in the rocks outside of the deposit are sparse, and those found have proved to be two-phase relatively dilute solutions that homogenize at temperatures below 450°C (J. T. Nash, written

commun., 1971, 1972; M. J. Logsdon, oral commun., 1973). These observations are similar to other calc-alkaline igneous suites and they suggest to us that the Laramide magmas near Ray did not release much water at magmatic temperatures during their solidification. Thus, additional petrologic and chemical studies outlined below were conducted to determine how Cu, S, Cl, F, and H₂O behaved during development of these intrusive rocks (Banks, 1976, N. G. Banks, unpub. data).

In contrast to the fracture-localized sulfide minerals in the deposit, the Laramide igneous rocks outside of the deposit contain sulfides that predominantly occur as inclusions in the earlier formed silicates and magnetite. Modally, these sulfide minerals become progressively less abundant, their pyrite to copper sulfide ratio increases as the host rocks become more felsic and younger, and their distribution in the host minerals suggests that saturation of sulfur in the melts was local rather than general. Additionally, the sulfur contents of apatite, biotite, and hornblende in the samples do not indicate a trend with increasing differentiation index or decreasing age of the sample. Likewise, copper which was only rarely detected in the nonsulfide igneous minerals by both electron and ion microprobe analyses, does not indicate a trend of copper enrichment or depletion in the minerals with indicators of rock differentiation. The same observation was made for mineral separates and rock samples analyzed by emission spectroscopy.

The above observations hold true both for samples representing an individual stock and for samples representing the entire igneous suite. Calculations using the modal abundance and sulfur and copper contents of the sulfide inclusions and other igneous minerals indicate that the less differentiated (older) Laramide rocks contain more sulfur than the more felsic (younger) rocks; no trend is indicated for the copper because of its erratic occurrence in silicates and oxides. The distribution of sulfur is explained by us as the result of its progressive consumption by the igneous minerals from a melt that was only locally saturated with respect to sulfur. The copper and sulfide data indicate that very little copper of igneous origin occurs in the rocks and that the activity of copper in the melts decreased during development of the Laramide rocks. These interpretations of the data are simple and adequate petrologically but conflict with the "classical magmatic model," which would be better supported by an enrichment of copper and sulfur in the younger magmas. Therefore, if the exposed stocks reflect processes that occurred in a presumed buried batholithic parent to the deposit, the activity of sulfur in the assumed parent body did not increase regularly with differentiation, and most of the copper in the batholith separated as sulfides that were armored by silicates and magnetite. Any aqueous phase released from or introduced into the batholith thus must have had restricted access to the richest copper source in the magma. Therefore, if the "classical magmatic" or "meteoric water" models are used to explain Ray, then the exposed stocks are not representative of the parent batholith either because of reasons unknown, or because of processes that changed their character between their separation from the parent and their solidification.

Changes in the character of the daughter magmas have been postulated to result from progressive removal of the copper and sulfur by way of an aqueous phase. However, the data on the behaviour of the Cl, H₂O, and F in the magmas at Ray impose strong restrictions on this postulate (Banks, 1976). For example, the abundance of Cl, F, and H₂O in apatite, biotite, hornblende, and sphene correlate consistently (although in varying degree) with changes of chemistry and age of the rock sample. The concentrations of chlorine, fluorine, and water in Laramide plutonic rocks associated with the deposit decrease or remain the same as rocks become more felsic and younger. Within igneous hydroxyl-bearing minerals in the rocks, chlorine and water contents decrease or remain the same as the host rocks become more felsic, and they decrease as the rock becomes younger. Fluorine, on the other hand, becomes more abundant in the igneous hydroxyl-bearing minerals as the rocks become more felsic and younger. These relations were observed for the igneous series as a whole and for one pluton with a range of texture, mineralogy, and composition similar to the entire igneous series. In contrast, the Cl, F, and H₂O contents of the minerals do not show trends with respect to grain size, grain shielding (by virtue of inclusion in different hosts), degree of alteration of the rocks collected outside of the commercial deposit, or to proximity of the analyzed spot to grain edges. Such relations suggest that the hydroxyl-bearing minerals retain an imprint of magmatic events. Thus, it seems reasonable to postulate that the trends in the mineral contents of Cl, F, and H₂O were caused by changes in the activities Cl⁻, F⁻, and OH⁻ in the magmas and that (analogous to variations in Na, Si, Al, and Ca in plagioclase) the changing relative activities of these ions in the melts was caused by their removal by the hydroxyl-bearing minerals. This explanation of the trends is simple and adequate, petrologically, and is compatible with the fact that water and chlorine are much less soluble than fluorine in silicate melts (Koster van Groos and Wyllie, 1968, 1969; Wyllie and Tuttle, 1964; Burnham, 1967), suggesting that the first formed minerals should tend to incorporate more chlorine and water than later formed minerals which would form in melt enriched in fluorine relative to the chlorine and water. Given this interpretation of the observed trends and the presence of hydroxyl-bearing minerals in aplites of the stocks, it is a reasonable postulate that most of the Cl and water in the stocks (and by analogy, any assumed parent batholith) were utilized by igneous minerals and that the stocks (and batholith) did not release much chlorine-rich water.

The above does not imply a unique explanation to the observations. Without data to the contrary, the presence of a special magma just below the Ray cannot be ruled out. Likewise, although we favor the above explanations for the trends observed for Cu, S, Cl, F, and H₂O, the data do not prohibit a late buildup of chlorine-rich water in a buried crustal batholith. That is, one might still postulate that Cu, S, and Cl were removed from the exposed stocks by escaping water. However, special conditions must then be applied (Banks, 1976).

One special condition is that if water escaped the magma, it did so without generating copious aplitic and pegmatitic dikes, large thermal aureoles, miarolitic features, and fluid inclusions in expected numbers and of the expected filling temperatures. In other words, water was released without leaving physical evidence of its former presence. Another is required by the observed progressive fluorine enrichment in the biotite of progressively younger and more felsic rocks (Banks, 1976). Because the Mg content of the biotite in the younger rocks is less than the Mg content of biotite in the older rocks and because a progressive decrease in magma temperature can be reasonably assumed for the progressively more felsic magmas, experimental and theoretical data predict that biotite in water-evolving magmas should have incorporated more F in the older more mafic magmas than the younger and more felsic ones (Munoz and Eugster, 1969; Ludington, 1973; Munoz and Ludington, 1974). The observed trend, which is opposite that expected for magmas that evolved water, is not explained by an increase in f_{O_2} of the magma because the modal abundance of magnetite in the Ray rocks decreases with decreasing age and increasing differentiation index of the rocks and because Fe/Fe+Mg content of biotite and hornblende in the Ray rocks increases with differentiation (see Wones and Eugster, 1965). Likewise, an increase in F content of the (assumed) evolving water is not easily applied to explain the trend because F is more soluble in hotter water (Munoz and Eugster, 1969). Additionally, because biotite is known to readily exchange fluorine and water with an aqueous phase at magmatic temperatures (Munoz and Eugster, 1969; Munoz and Ludington, 1974), the F trend for biotite and the observed measurably different F contents of biotite grains in the same rock and even thin section are not easily discounted by postulating slow kinetics but instead would seem to imply (in agreement with the geologic observations) that very little water had contact with the biotite at magmatic temperatures. Therefore, if one postulates that the magmas at Ray evolved much water during their ascent from the parent batholith, one must also postulate that the wallrocks, the igneous rocks, and the igneous biotite did not record the event.

Finally, the interstitial and crosscutting textural relations of the hydroxyl-bearing minerals in the main rock types and also their presence in aplites indicate that hydrous minerals continued to form late in the crystallization history of the stocks (Banks, 1976). These stocks were emplaced at depths ranging from 1.5 km or less to 3 km or more (Banks and others, 1972; Banks and Stuckless, 1973). At these depths melts should saturate at between 2.5 and a little more than 3.5 weight percent water (Burnham, 1967), or at, or slightly above, the approximate amount required in the melt for biotite formation (Wones and Eugster, 1965; D. R. Wones, oral commun., 1973). Therefore, if one postulates that Cu, S, and Cl were removed by evolution of water, disequilibrium crystallization of the exposed stocks may have to be postulated because the formation of biotite and the other hydrous minerals would have tended to control the contents of Cl, F, and H₂O in the ascending magma and inhibit buildup of water in the magma.

Thus, in addition to the general problems that both the "classical magmatic" and circulating groundwater models have for the origin of the Ray deposit, the classic magmatic model appears because of observational data on the plutons to require enough new special conditions to warrant entertainment of an alternative hypothesis that might explain the generation of the Ray and perhaps other porphyry copper deposits while still maintaining the apparent time-space relation between the deposits and calc-alkaline magmatism.

A tectonic or deep-seated source dependence of porphyry copper generation is suggested to us because calc-alkaline magmatism and porphyry copper deposits seem to be concentrated in certain crustal areas (Noble, 1970, 1974; and others). Particularly for Ray, there seems good evidence that during Laramide time, the southwestern part of Arizona was subjected to roughly east-west regional compression with attendant north-south tension, inasmuch as both dike swarms and sulfide veinlets occupy the east-west features (Rehrig and Heidrick, 1972). In the Ray area this east-west orientation of veinlets and dikes is well developed, and many of the dikes are less than 3 m wide and have penetrated at least 600 m of carbonate rocks. Hence, they could not have stopped their way to their present level. We speculate that this regional east-west compression could have resulted from movement of lithospheric plates and therefore suggest that plate tectonics is somehow involved in porphyry copper generation, and we also suggest that the plutons are products of partial melting. Neither suggestion is new (Guilbert and Sumner, 1968; Sawkins, 1972; Sillitoe, 1972; Noble, 1970, 1974; Livingston, 1973; and others). However, the type of tectonics responsible is not critical to us for it appears to be regional, and the resulting zones of weakness were conduits for deep-seated magma. Whether the assumed melting was induced by moving oceanic crust along a subduction zone (Sillitoe, 1972) to a hotter environment (perhaps aided by friction), or whether heat for melting was supplied by a mantle hot spot (Livingston, 1973), or another as yet unformulated mechanism does not concern us. We have abundant evidence that the heat was available and that magmas were generated at the proper time.

Strontium isotopic data on the plutons (Moorbath and others, 1967; Livingston, 1974) seem adequately explained by partial melting of oceanic crust (Sillitoe, 1972) or by mixing of partly melted continental crust with basalt (Livingstone, 1974). The problem is that experimental work (for example, Winkler, 1957, 1958, 1960, 1965; Winkler and von Platen, 1958) and field observations have concentrated on the behavior of the major silicates during partial melting, and relatively little data are available that describe the behavior of sulfur and base metals under anatexis conditions. Some evidence concerning their behavior may be inferred from experimental studies by MacLean (1969) and Shamazaki and Clark (1973), and from descriptions of sulfide minerals in xenoliths from basalts given by Frick (1973) and de Waal and Calk (1975). More importantly, the partly melted country rocks near the Precambrian Stillwater Complex, Mont., appear to offer observational data that are applicable to the Ray problem.

Stillwater Complex.--Discontinuous, isolated lenses and veins of quartz norite, as much as 5 cm wide, occur below the Stillwater Complex in hornfelsed metasedimentary rocks of Precambrian age. The hornfels have the mineral assemblages orthopyroxene-cordierite-biotite and green spinel-cordierite (Page and Nokleberg, 1970, 1972a, b). The quartz norite lenses are widespread along the projected trend of the complex, and they extend outward from the base of the complex to a maximum distance of 300 m into the metasedimentary rocks. Within the areas where these lenses are developed, they compose between 1 percent and 10 percent of the exposed rocks. Similar rocks ascribed to partial melting or fusion of country rocks associated with mafic intrusive rocks in northeast Scotland have been described by Gribble (1966, 1967, 1968, 1970) and Gribble and O'Hara (1967); other localities are described by Wyllie (1959) and Agrell (in Chinner and Schairer, 1962, p. 633).

The quartz norite lenses resemble the products expected from partial fusion of the metasedimentary rocks at temperatures near the melting point of basaltic rocks. The logical heat source for such fusion is the Stillwater magma; mineral assemblages are comparable with the phase relations found experimentally by Schairer and Yoder (1970, p. 212), Chinner and Schairer (1962), and Hytoñen and Schairer (1960) in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. The experimental studies show that liquids with compositions of quartz norite and norite could be derived from rocks with the compositions of the metasedimentary rocks near the Stillwater by heating to temperatures of about 1150-1200°C; at higher temperatures, other liquids with bulk compositions of cordierite-norite could form. Such a process, and perhaps only this process, would explain the discordant and concordant isolated lenses of quartz norite in the country rock of the Stillwater that contain euhedral orthopyroxene phenocrysts. The orthopyroxene most likely crystallized from a melt--on the basis of its textural and optical similarities with orthopyroxene in the complex--and is enclosed in a quartz and plagioclase matrix that locally exhibits a micrographic texture or is composed of vermicular intergrowths.

Two characteristics of the quartz norite lenses are attractive features for hypotheses concerning porphyry copper generation: (1) the rocks derived by partial fusion near the Stillwater Complex contain up to 3 percent biotite and, in other examples, primary amphibole (Gribble, 1967), indicating that water enters partial melts; and (2) macroscopic amounts of chalcopyrite, pyrrhotite, and pentlandite are concentrated in, near, and around the lenses. We speculate here that an aqueous phase (intergranular or otherwise) was present and that the water with dissolved sulfide components was attracted to the undersaturated melt; some part of the constituents entered the melt, but more significantly, because of the low solubility of sulfur in mafic silicate melts (Haughton and others, 1974) most of this material precipitated near the hornfels-quartz norite contacts.

THE MODEL

In view of the observations and the interpreted behavior of fluids and metals in partially melted country rock below the Stillwater Complex, we propose a model of porphyry copper generation that is compatible with the behavior of H_2O , Cu, S, Cl, and F in the Ray rocks and that also fits previously published experimental and observational data. We postulate that partial melting occurred near or below the base of the crust in Arizona during Laramide time and that insufficient H_2O was available to achieve or maintain melt saturation. The water, carrying dissolved Cl and F, migrated along chemical potential gradients toward the undersaturated melt. This migrating fluid carried sulfide components as either chloride complexes (Garrels, 1941; Helgeson, 1964) or perhaps as sulfide complexes (e.g., Barnes and Czamanske, 1967). As proposed for the Stillwater example, most of the sulfur, copper, and some iron and other base metals are postulated to have remained at or near the melt contact as the F, Cl, H_2O entered the magma, resulting in a concentration of metal sulfides in the melt zone around pockets of magma but because of low sulfur solubility in silicate melts *not in the magma*. With a continued supply of heat, sulfide concentrations would increase around the continually growing pockets of melt, and eventually some of the pockets of melt would coalesce and come in contact with zones of structural weakness.

At Ray, a magma of tonalitic composition was first to arrive at the proper volume and consistency for mobilization, transportation, and emplacement at shallow depths. Probably insufficient H_2O was incorporated in the Ray magmas to achieve or maintain saturation because of original paucity in H_2O content of the country rock or because of the relative rates of melting and H_2O migration and diffusion. Thus, the magma leaving the zone of melting had none of the problems that a water-saturated or water-saturating magma (Luth, 1969; Burnham, 1967) might have in arriving at the required levels in the crust. Water saturation resulting from decreasing total pressure in the ascending magma was averted or alleviated by the crystallization of hydroxyl-bearing phases from the magma. Therefore, relatively little or no heat was lost through an aqueous phase escaping from the ascending batches of magma.

Water for leaching and transport of the ore components concentrated in the zone of melting may have been derived both by metamorphic dehydration and by cooling and crystal differentiation (except for depth, identical to the "classical magmatic model") of some of the remaining pockets of magma (particularly those surrounded by or below sulfide accumulations) at conditions not favorable to total consumption of Cl, F, and H_2O in the melt by precipitating minerals. These conditions might have been brought about by (1) disequilibrium crystallization of the melt, (2) deficiencies in some of the melts of major elements required to form hydroxyl-bearing minerals stable at the temperature

of crystallization, (3) insufficient amounts of Cl, F, and H₂O in the melts to allow attainment of appropriate activities to form ²hydroxyl-bearing minerals at the pressure and temperature of crystallization of the melts, or (4) upward migration of nearly saturated magma within the zone of melting. Thus, in our model it was an aqueous phase, rather than a magma, that was enriched in sulfide components in the zone of melting. We again acknowledge that we are not alone in postulating that an aqueous phase from depth forms ore deposits (e.g., Barsukov and Dimitriev, 1972; Dodge, 1972; Corliss, 1973; Noble, 1970, 1974; many others). Our model differs in providing a concentrated Cu-S source at or above sites of water production at depth. Whether or not the waters remained ore bearing to exposed levels would depend at least partly on the pressure on the fluid and the temperature of the conduits. Thus, it is probable that transportation of ore into the porphyry environment might be episodic, require several steps of mobilization, and require the closeness in time and space of a previously emplaced pluton or dike swarm.

The ultimate source of the metal and sulfur is unknown. However, because basaltic rocks contain about five times more copper than granitic rocks (Turekian and Wedepohl, 1961), the process would have been aided by the presence of mafic rocks or rocks derived from mafic rocks. The ultimate source of the water could be pore and structural water released by prograde metamorphism.

The model that the sulfide components for porphyry deposits (and perhaps other base metal deposits) accumulate in melt zones during anatexis and move to an upper crustal site via an aqueous rather than a magmatic phase is presented as another end-member model that must inevitably change or be combined with other models to accommodate future observations and experimental data. Furthermore, the model need not apply to every deposit or every region. However, it has exploration applications because it implies a structural control for at least some porphyry-type deposits and suggests that the presence of an upper crustal calc-alkaline pluton may not be a required criterion for prospecting.

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DISTRIBUTION OF COPPER IN BIOTITE AND BIOTITE ALTERATION PRODUCTS IN INTRUSIVE ROCKS NEAR TWO ARIZONA PORPHYRY COPPER DEPOSITS

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Abstract.—Biotite and its alteration products (primarily chlorite) from igneous rocks around the Ray and Esperanza (Esperanza-Sierrita) porphyry copper deposits, Arizona, were analyzed for copper by electron microprobe. The copper occurs in amounts >90 p/m (limit of detection) in most of the chlorites analyzed, is concentrated at the optical and chemical boundary of chlorite and biotite, and is not associated with sulfur. Most unaltered igneous and hydrothermal biotites analyzed contain <90 p/m Cu, and except for one sample, all copper that was detected can be explained as contamination by copper from chlorite grains. The paucity of detectable copper in igneous and hydrothermal biotite and its presence in daughter chlorite suggest that the positive association noted by some workers between the proximity of an ore deposit and the copper content of biotite might be partly the result of increased amounts of chloritization of biotite near a deposit coupled with difficulty in physically cleaning the biotite separates. Additionally, previous speculations that (1) part of the copper in a deposit may come from altered biotite, and (2) copper in biotite indicates how copper behaves in a differentiating magma, are of doubtful value if based on data derived from analyses of bulk mineral separates.

The copper, sulfur, and major-element contents of biotite and its alteration products from igneous rocks associated with the Ray and Esperanza (Esperanza-Sierrita) porphyry copper deposits were determined by microprobe analyses. The results do not agree with some of the published data about the distribution of copper in biotite nor with some of the speculations drawn from that data.

The Ray samples, collected 2–11 km from the deposit, consist of 2 ore specimens and 21 igneous rocks representing 5 intrusive types. All five intrusive types are cut by sulfide-bearing veinlets in and around the Ray deposit. The deposit is located about 120 km north of Tucson, Ariz. The intrusive rocks temporally associated with the deposit range in composition and texture from hornblende diorite (andesite) to quartz monzonite (quartz latite) (Cornwall and others, 1971; Banks and others, 1972). Intrusion began about 70 m.y. ago and continued to about 60–61 m.y. ago—the Laramide age of the youngest intrusive body (Granite Mountain Porphyry) within the commercial limits of the deposit (Creasey and Kistler, 1962; Banks and others, 1972; Banks and Stuckless, 1973). Sulfide mineralization followed, and the deposit cooled below

100° C about 60 m.y. ago (Banks and Stuckless, 1973).

The Esperanza deposit, about 40 km south of Tucson, is associated with the Ruby Star Granodiorite, also Laramide in age (Creasey and Kistler, 1962; Damon and Mauger, 1966). T. G. Lovering kindly supplied igneous biotite, separated from seven samples collected from this intrusive body, 0.8–4 km from the center of mining activity at Esperanza.

ANALYTICAL METHODS

Extreme care was taken to eliminate contamination of copper by external sources. Rock chips (Ray samples) and mineral grains (Esperanza samples), plastic mounted onto glass slides and cut to 40- to 50- μ m thickness by diamond saw, were ground and polished on glass plates in several steps, using diamond powder as an abrasive to remove any copper smeared onto the specimens from brass in the saw blade. Between each step, the slides were agitated in an ultrasonic cleaner, then positioned so that the direction of polishing was 90° from the previous direction. Finally, the slides were polished four more times on nylon over glass with alumina powder, agitated in an ultrasonic cleaner, and again rotated 90° between each polishing step.

Several mounts were polished on a lead-bronze lap with diamond powder, analyzed, repolished by use of the four-step alumina method, and finally reanalyzed to check if any copper physically smeared onto the sample was actually removed by the polishing with alumina. Copper in erratic but measurable concentrations (parts per million) was detected on some biotite grains in the slides polished on the lead-bronze lap (not on well-polished nonlayer silicates) but was not detected on the same grains after the alumina polishing. Thus, sample contamination by copper sources external to the sample is believed to have been eliminated by this polishing.

Contamination of minerals by copper from other minerals in the slide could not be eliminated. However, the sources of contamination are identified, and as explained later, the contamination does not alter the conclusions drawn here.

The copper and sulfur analyses were made with an ARL (Applied Research Lab.) model EMX-SM electron microprobe

using a LiF crystal for copper and an ADP crystal for sulfur, an excitation voltage of 20 kV, a sample current of 3×10^{-8} A on brass, and chalcocite (Cu_2S) as a standard. Integration times of 200 ± 2 s were obtained by termination of counting on fixed-beam current. For most analyses 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 as much as 10 by 8 μm . If the shape of the grain did not permit sweeping of areas of at least 5 by 4 μm , a defocused beam (2–3 μm diam) was used, and the sample was moved under the beam about once every 20 s.

X-ray intensity data (counts) were obtained by averaging 2–40 (usually 6–8) observations on each grain. Initially, correction of the raw intensity data was done by computer and included drift, background, and matrix corrections (mass absorption, secondary fluorescence, and atomic number effects; Beeson, 1967; Beaman and Isasi, 1970). Individual backgrounds for each grain were determined by observing counts above and below the peak wavelengths of copper and sulfur. Major-element data required for the corrections and data in table 3 and figures 6 and 7 were obtained at an excitation voltage of 15 kV and count times of 20 ± 0.5 and 40 ± 1 s. It developed, however, that the computer correction factor for trace amounts of copper and sulfur (50–5,000 p/m) is nearly constant for each mineral type studied regardless of its exact major-element composition. Thus, in the later part of the study and for most of the data on tables 1 and 2, a matrix correction for copper and sulfur in each mineral type (derived in the initial study) was applied by hand. During this stage of the study, usually magnesium or potassium was monitored as a check on the purity of the mineral grains.

A homogeneous synthetic glass containing about 400 p/m Cu and 520 p/m S was repeatedly analyzed under the above operating conditions. The one standard deviation of error from the average amount of copper present in the glass was 10 percent (8 percent for S), and the maximum deviation was 20 percent (15 percent for S). Detection levels were established at three times the square root of the average background counts (Birks, 1963); thus, copper is considered detectable at about 90 p/m (50 p/m for S) at the above operating conditions in the minerals analyzed.

COPPER AND SULFUR CONTENTS OF THE MINERALS

The copper and sulfur contents of hydrothermal biotite from the Ray deposit and of igneous biotite and its alteration products (chlorite, epidote, sphene, and hydrogarnet?) from five intrusive rock types located near the deposit are listed in table 1. Similar data for igneous biotite and its alteration products from the Ruby Star Granodiorite near the Esperanza deposit are presented in table 2.

Chlorite formed by alteration of biotite near both the Ray

and Esperanza deposits contains significantly more copper than the unaltered igneous biotite analyzed (fig. 1). Most of the biotite grains (80 percent of the Ray and 75 percent of the Esperanza biotite), including those of hydrothermal origin, do not contain detectable amounts of copper, whereas 65 percent of the Ray chlorite grains analyzed and 90 percent of the Esperanza chlorite grains analyzed contain detectable amounts of copper.

LOCATION OF COPPER IN CHLORITE

Sulfur and copper in the biotite and chlorite were monitored during the analyses on a memory oscilloscope or on Polaroid film over a nonrecording oscilloscope to determine whether sulfide or sulfate inclusions might account for the copper in the chlorite or biotite. With one possible exception (a chlorite grain in sample 2GM14, not listed in table 1), no such inclusions were found. Furthermore, it is unlikely that the copper is present in sulfide or sulfate grains that are smaller than can be detected on the oscilloscope because increases in the amount of copper in either biotite or chlorite are not accompanied by corresponding increases in the amount of sulfur (fig. 2). For example, the ratio of copper to sulfur should be 1 to 1 if the copper were present in chalcopyrite inclusions and 4 to 1 if the supposed inclusions were chalcocite; these ratios are not found (fig. 2). In addition, several quantitative analyses for Mo, Zn, Pb, Mn, Cl, and F (by microprobe) indicate that the copper in the grains also is not associated with these elements. The presence of copper carbonates or nitrates was not checked directly because the sections were carbon coated, and an analyzing crystal suitable for nitrogen analyses was not immediately available. A direct check for the presence of copper silicates and an indirect check for the presence of copper carbonates, oxides, and nitrates by analyzing the grains for silicon and oxygen was not possible because the copper occurs in a silicon-oxygen matrix (biotite and chlorite) having approximately the same silicon or oxygen contents as the known copper carbonates, oxides, nitrates, and silicates. Thus, any variations in silicon or oxygen intensity data caused by the presence of minute quantities (parts per million range) of these minerals would be masked by analytical uncertainty in such data. Quantitative analyses for Se, W, As, Sb, Te, I, V, and P (the other elements occurring in known copper-bearing minerals) were not made, but qualitative scans were. As noted in the tables, the copper in chlorite is often distributed inhomogeneously and, as discussed below, is locally concentrated in sufficient quantities so that X-ray images of its distribution can be observed on and photographed from an oscilloscope. Similarly, if Se, W, As, Sb, Te, I, V, or P were present in amounts comparable to the copper, they could be observed on the X-ray images; they were not.

Table 1.—Copper and sulfur in biotite and its alteration products from the intrusives near the Ray porphyry copper deposit, Arizona

[Values in regular type denote element is present at or above detection level (about 90 p/m for Cu and 50 p/m for S). Values in italic type indicate real or fictitious element contents resulting from higher-than-background counts at the peak wavelength of the element. Copper and sulfur values are not significant to three figures. Precision is lower in grains in which copper and sulfur are not homogeneously distributed]

Rock type	Sample	Grain	Mineral	Copper (p/m ±10 percent)	Sulfur (p/m ±10 percent)	Rock type	Sample	Grain	Mineral	Copper (p/m ±10 percent)	Sulfur (p/m ±10 percent)
Tortilla	217-1	1BI	Biotite	0				5CL	.. do ..	0	0
Quartz		2BI	.. do ..	0				1EP	Epidote	0	0
Diorite.		3BI	.. do ..	0	138			4EP	.. do ..	0	0
		5BI	.. do ..	0	161	Rattler	260-113D	2BI	Biotite	0	189
		2CL	Chlorite	0		Grano-		3BI	.. do ..	0	256
		4CL	.. do ..	42	20	diorite-Con.		4BI	.. do ..	0	190
		5CL	.. do ..	16	0			5BI	.. do ..	0	254
		6CL	.. do ..	0	0			3CL	Chlorite	0	0
		7CL	.. do ..	24	23			4CL	.. do ..	0	0
		6EP	Epidote	42	52			3M	Hydrogarnet?	0	0
		7EP	.. do ..	0	0			1EP	Epidote	0	0
	217-28	1BI	Biotite	386*	167		246-11A	5EP	.. do ..	0	15
		3BI	.. do ..	39	199			1BI	Biotite	256*	
		4BI	.. do ..	52				1BIA	.. do ..	245	
		5BI	.. do ..	109				2BI	.. do ..	0	313
		BTM1	.. do ..	21	199			4BI	.. do ..	405*	
		1CL	Chlorite	206*	59			5BI	.. do ..	57	294
		2CL	.. do ..	244*				5BIA	.. do ..	119*	
		4CL	.. do ..	149	86*			BIM1	.. do ..	496*	280
		5CL	.. do ..	120	45			BIM2	.. do ..	0	282
		4M	Hydrogarnet?	151*	79			1CL	Chlorite	2218*	21
		3EP	Epidote	40	28			1CLA	.. do ..	1368	
	248-29	2CL	Chlorite	60				3CL	.. do ..	460	14
		3CL	.. do ..	190				3CLA	.. do ..	2000*	10
Rattler	246-99B	3BI	Biotite	697	172			4CL	.. do ..	405	
Grano-		1CL	Chlorite	569	74			4CLA	.. do ..	3138*	
diorite.		2CL	.. do ..	432	50			4CLB	.. do ..	617	
	46-11G	BI	Biotite	0				5CLA	.. do ..	2397*	
		CL	Chlorite	2237				5CLB	.. do ..	4118*	
		EP	Epidote	2000*				5CLC	.. do ..	8340*	
	246-11G	1BI	Biotite	26				CLM1	.. do ..	1432*	20
		3BI	.. do ..	28	199			CLM2	.. do ..	9842*	0
		4BI	.. do ..	0	181		260-96A	1BI	Biotite	52	214
		7BI	.. do ..	110	146			3BI	.. do ..	0	191
		BTM1	.. do ..	0	197			4BI	.. do ..	0	220
		1CL	Chlorite	626				5BI	.. do ..	0	185
		5CL	.. do ..	51	1			2CL	Chlorite	754*	254
		6CL	.. do ..	105	0			2CLA	.. do ..	416	262*
		CLM1	.. do ..	0	10			3CL	.. do ..	1160*	54
		CLM2	.. do ..	0	6			6CL	.. do ..	674*	112*
		2EP	Epidote	10	41			1EP	Epidote	608*	22
		6SP	Sphene	53	82*			6SP	Sphene	94	0
	61-25	BIGM	Biotite	0		Rhyodacite	2GM100	1BI	Biotite	51	290
		BI1	.. do ..	0		dike		2BI	.. do ..	36	243
		BI2	.. do ..	0				3BI	.. do ..	15	274
		CL2	Chlorite	291				2CL	Chlorite	0	44
		EP2	Epidote	157				4CL	.. do ..	102	105
	261-25	1BIA	Biotite	0	209			5CL	.. do ..	66	117
		1BIB	.. do ..	0	283			4EP	Epidote	0	0
		3BI	.. do ..	0	184			5EP	.. do ..	130*	0
		5BI	.. do ..	0	156			4SP	Sphene	0	0
		2CLA	Chlorite	0	0			5SP	.. do ..	0	0
		2CLB	.. do ..	0	0	Granite	GM14	BI	Biotite	0	
		4CL	.. do ..	0	5	Mountain		CL1	Chlorite	0	
						Porphyry.					

Table 1.—Copper and sulfur in biotite and its alteration products from the intrusives near the Ray porphyry copper deposit, Arizona—Continued

Rock type	Sample	Grain	Mineral	Copper (p/m±10 percent)	Sulfur (p/m±10 percent)	Rock type	Sample	Grain	Mineral	Copper (p/m±10 percent)	Sulfur (p/m±10 percent)
Granite	GM14	CL2	.. do ..	582		Granite	2GM6GR	4BIM	.. do ..	0	
Mountain		CL3	.. do ..	34		Mountain		3CLM1	Chlorite	261	
Porphyry—		EP	Epidote	0		Porphyry—		3CLM 2	.. do ..	442	
Con.		SP6	Sphene	0		Con.		4CLM	.. do ..	125	
	2GM11	1BI	Biotite	20	311		3GM6G	B11	Biotite	0	
		2BI	.. do ..	0				B12	.. do ..	0	
		2B1A	.. do ..	0	202			B13	.. do ..	0	
		3BI	.. do ..	198	273			CL1	Chlorite	385	
		4BI	.. do ..	0	237			CL2	.. do ..	382	
		6BI	.. do ..	0				CL3	.. do ..	414	
		BTM1	.. do ..	0	158		2GM4V	B1B	Biotite	110	
		2CL	Chlorite	110	0			1B1A	.. do ..	0	
		5CL	.. do ..	42	11			3B1A	.. do ..	0	
		6CL	.. do ..	5	68			3B1B	.. do ..	0	
		CLM1	.. do ..	79	75			1CL	Chlorite	915*	
	GM12R	2B1X	Biotite	0	208			1CLA	.. do ..	818*	
		3BI	.. do ..	111	237			3CL	.. do ..	105	
		3B1A	.. do ..	144	180		2GM1A	2CL	.. do ..	324	
		1BI	.. do ..	110	156			2CLA	.. do ..	275	
		5BI	.. do ..	125	152			2CLB	.. do ..	311	
		3CL	Chlorite	699	26			CLM	.. do ..	1537*	
		3CLA	.. do ..	294	26	Teapot	TTM	ICL	Chlorite	1235*	
		4CL	.. do ..	297	44	Mountain		3CL	.. do ..	1172*	
		5CL	.. do ..	527	98	Porphyry.		CLM1	.. do ..	1006*	
	GM6GR	B11	Biotite	0				1SP	Sphene	145	
		B1A	.. do ..	0				3SP	.. do ..	124	
		3B1A	.. do ..	0	120	Hydro-	2P70-22	1BI	Biotite	80	90
		4B1A	.. do ..	0	190	thermal		2BI	.. do ..	46	486
		3CLA	Chlorite	3440*	0	biotite.	T123R	B11	Biotite	26	189
		4CLA	.. do ..	80	0			B12	.. do ..	37	113
		CLA	.. do ..	266				B13	.. do ..	64	156
	2GM6GR	2B1M	Biotite	0	190			B14	.. do ..	30	197
		3B1M	.. do ..	0				B15	.. do ..	33	191

*Element not distributed homogeneously in the grain. Criterion used was whether standard deviation from mean of counts divided by the square root of the average counts is >3 (Boyd, 1969).

The copper reported for chlorite in tables 1 and 2 was probably not smeared over the chlorite from other copper-bearing phases in the mounts because (1) the distribution of copper in the chlorite (discussed next) precludes such a source, (2) the copper content of the chlorite grains does not reflect the proximity, size, or even presence of copper sulfides in a given slide (always <200 p/m including chalcopyrite), and (3) except for sample 246-99B (table 1), copper was not found in other igneous silicate, oxide, or phosphate phases in the samples in amounts equal to or greater than that found in chlorite. Contamination of the chlorite with copper from chalcopyrite in veinlets was avoided by using probe mounts that contain no veinlets.

The amount of copper in chlorite is highest near the chlorite-biotite contact. Chlorite more than $50 \mu\text{m}$ from the

mineral contact contains about 600–1,000 p/m Cu, biotite more than $50 \mu\text{m}$ from the contact contains copper in amounts just at or below the detection level, and about 1.5 percent Cu is found in the chlorite at the mineral contact (fig. 3A, sample 2GM4V, grain 1 CL). The amount of copper (about 1.5 percent) at the mineral contact is probably low because the material excited by the beam and secondary radiation extends beyond the visible mineral contact. Likewise, the broadness of the copper peak (fig. 3A) may be partly the result of excitation of copper in the contact zone by secondary radiation from points located in chlorite and biotite near the mineral contact.

The concentration of copper in chlorite along another biotite-chlorite boundary is shown as X-ray images photographed from an oscilloscope (fig. 4). The chlorite contains about

Table 2.—Copper and sulfur in biotite and its alteration products from Ruby Star Granodiorite near the Esperanza porphyry copper deposit, Arizona

Values in regular type denote element is present at or above detection level (about 90 p/m for Cu and 50 p/m for S). Values in italic type indicate real or fictitious element contents resulting from higher-than-background counts at the peak wavelength of the element. Copper and sulfur values are not significant to three figures. Precision is lower in grains in which copper and sulfur are not homogeneously distributed.]

Sample	Grain	Mineral	Copper (p/m, ±10 percent)	Sulfur (p/m, ±8 percent)	Chlorite in separate (percent)	Sample	Grain	Mineral	Copper (p/m, ±10 percent)	Sulfur (p/m, ±8 percent)	Chlorite in separate (percent)
T454R	BT5	Biotite	63	106	0.1	T467R	BTM4	Biotite	152	243	
	BTM1	.. do ..	0	180			BTM5	.. do ..	0	197	
	BT5A	.. do ..	0	139			CL1	Chlorite	766*	0	
	BT5C	.. do ..	0	138			CL2	.. do ..	3418*	0	
	BT5C1	.. do ..	0	125			CL3	.. do ..	3024*	7	
	CL5,	Chlorite	0	17			CLM1	.. do ..	1335	0	
T455R	BT1	Biotite	21	141	3.5		CLM2	.. do ..	1060	14	
	BT2	.. do ..	45	126		T468R	BT1	Biotite	49	201	12.4
	BT3	.. do ..	73	126			BT2	.. do ..	3	345	
	BT4	.. do ..	6	160			BT3	.. do ..	0	239	
	BT5	.. do ..	200*	87			BT4	.. do ..	0	221	
	CLM1	Chlorite	4758*	68			CL1	Chlorite	924*	0	
	CLM2	.. do ..	161	0			CL2	.. do ..	9700*	96	
	CL1	.. do ..	2040*	6			CL3	.. do ..	10,000*	36	
T465R	BT1	Biotite	0	69	0.7		CL4	.. do ..	4500*	32	
	BT2	.. do ..	145	119		T8R	BT1	Biotite	0	141	17.6
	BT3	.. do ..	0	156			BT2	.. do ..	616*	97	
	BTM1	.. do ..	0	140			BT3	.. do ..	0	167	
	BTM2	.. do ..	0	102			BT4	.. do ..	32	125	
	BTM3	.. do ..	0	125			BT5	.. do ..	129	109	
	CL1	Chlorite	175	20			CL1	Chlorite	403	0	
	SP1	Sphene	255	56			CL2	.. do ..	323*	16	
T467R	BT1	Biotite	654*	172	11.2		CL3	.. do ..	669*	0	
	BT2	.. do ..	511*	140			CL4	.. do ..	1656*	30	
	BTM1	.. do ..	28	275			CL5	.. do ..	429	10	
	BTM2	.. do ..	173	263			SP1	Sphene	57	23	
	BTM3	.. do ..	43	232			SP2	.. do ..	333	65	
							SP4	.. do ..	0	49	

*Element not distributed homogeneously in the grain. Criterion used was whether standard deviation from mean of counts divided by the square root of the average counts is >3 (Boyd, 1969).

5,000 p/m Cu at the mineral contact and about 500 p/m (average) away from it. Although sulfur counts were collected for longer times than the copper counts, corresponding sulfur counts (fig. 4C, F) are lacking where the copper is concentrated. Background sulfur in biotite (300 p/m) was not detected in figure 4C and F.

Figure 3B shows a paucity of copper in compositionally pure biotite, a high concentration of copper in chlorite at the compositional chlorite-biotite contact, and a decrease in amount of copper in chlorite as it becomes chemically purer (as demonstrated by loss of K). Thus, copper is both spatially and compositionally associated with the biotite-chlorite transition, which implies that the copper was introduced in the fluids that destroyed the biotite and formed the chlorite. The fact that other elements known to coexist in previously

described copper minerals were not concentrated with the copper suggests that the copper probably is present in either lattice or more loosely attached sites in the chlorite or other silicate minerals formed during transition of the biotite to chlorite. In the compositionally purer chlorite, the copper may be partly in exchangeable sites and partly in lattice sites. Dodge, Smith, and Mays (1969) and Parry and Nackowski (1963) point out that the radius of Cu^{+2} is appropriate for its camouflage in Fe^{+2} and Mg^{+2} (octahedral) positions. In the transitional material, the amount of copper present and the fact that cold concentrated nitric acid leaches copper from the Esperanza biotite-chlorite grains exposed in a rock-slab surface (T. G. Lovering, oral commun., 1972) might suggest a cation exchange position for part of the copper. The nature of the attachment of copper in this transitional material is discussed more fully in a later section.

COPPER IN BIOTITE AND BIOTITE ALTERATION PRODUCTS, ARIZONA

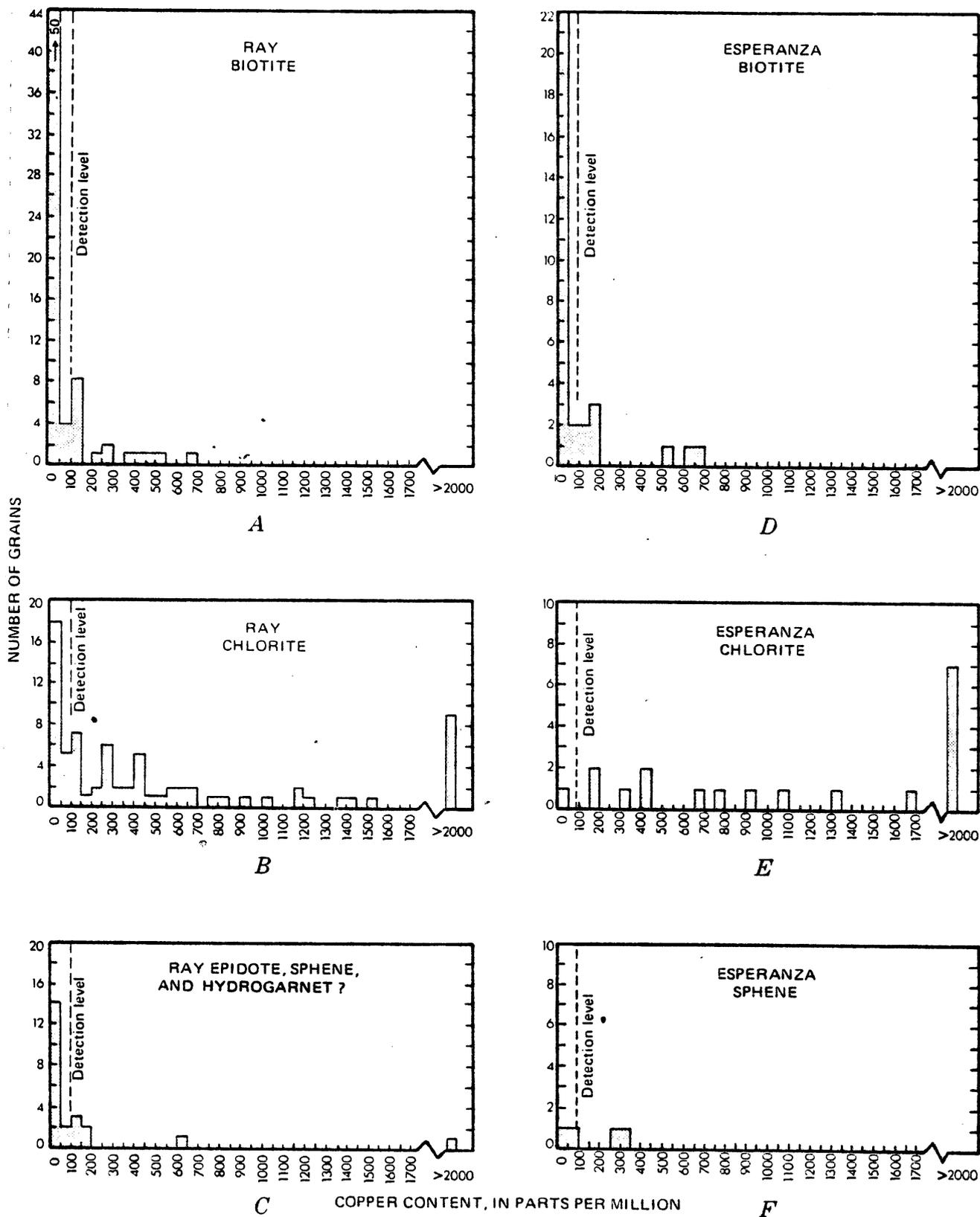


Figure 1.—Frequency histograms showing copper contents of biotite (*A* and *D*), chlorite (*B* and *E*), epidote, sphene, and hydrogarnet? (*C*), and Sphene (*F*) from Laramide intrusive rocks near the Ray and Esperanza copper deposits, Arizona. Detection levels established at three times the square root of the average background counts (Birks, 1963).

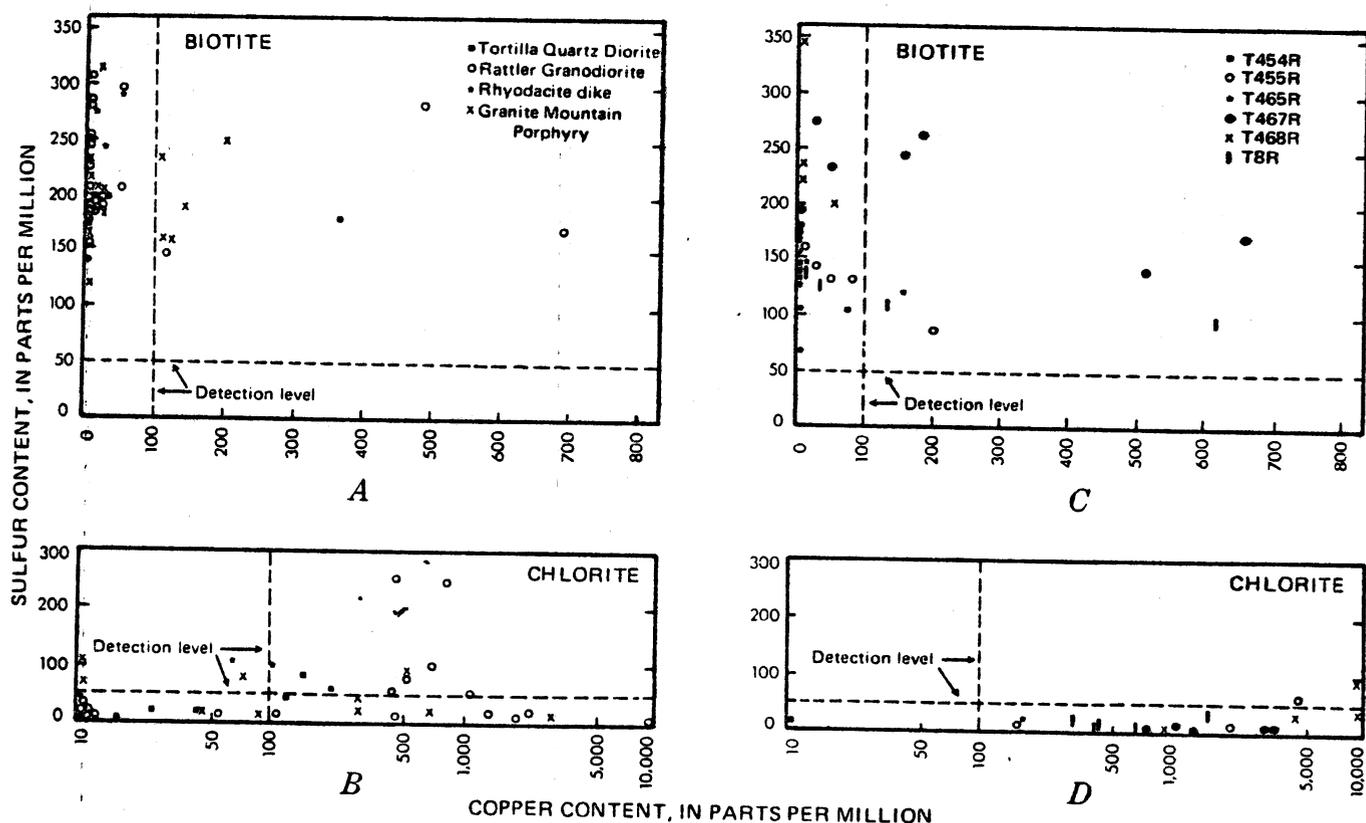


Figure 2.—Plots of copper versus sulfur contents of igneous biotite (A and C) and chlorite (B and D) derived from the biotite from rocks near the Ray and Esperanza copper deposits, Arizona. Note that different scales are used to plot copper in chlorite and copper in biotite. Three points from the Rattler Granodiorite and one from the Tortilla Quartz Diorite plot at the origin of B. Some points are slightly offset for plotting purposes. Detection levels were established at three times the square root of the average background counts (Birks, 1963).

CONTAMINATION ORIGIN FOR COPPER IN BIOTITE

The increase in copper content from parent biotite to daughter chlorite is probably even more striking than figure 1 shows because most biotite grains having detectable amounts of copper come from samples that contain chlorite having considerably more copper than the biotite. Thus part or all of the detectable copper reported for biotite may be copper from chlorite that has been smeared over the biotite during polishing. There is no simple relation between the degree of alteration of biotite in a sample and the presence or number of copper-bearing biotite grains analyzed in a sample. This is not surprising because the amount of copper smeared over the biotite would depend upon the proximity of copper-bearing chlorite, the amount of copper in the chlorite, and the position of a biotite grain relative to a copper-bearing chlorite and the final direction of polishing. However, the samples that have very little biotite alteration or that have no chlorite grains with detectable copper also have no biotite grains with detectable copper. In addition, biotite precipitated from copper-bearing fluids (hydrothermal biotite, table 1) does not contain

detectable copper except immediately adjacent to chalcopyrite (these analyses were not reported in table 1 because of likelihood of copper contamination from the sulfide). Therefore, it is likely that the igneous biotite (with the possible exception of sample 246-99B, grain 3BI) does not contain copper in amounts detectable by the probe and that the copper in all but one biotite reported in tables 1 and 2 may be best explained by autocontamination. The exception, sample 246-99B, grain 3BI, is not easily explained by contamination with copper from chlorite because only the two grains of chlorite, both completely chloritized with no biotite-chlorite contact, occur in the sample, and the biotite contains more copper than the chlorite (table 1). Copper in this biotite also is not easily explained by contamination with copper from sulfides because no chalcopyrite occurs in the probe sample, and the pyrite contains less copper (300 p/m) than the biotite. Hornblende in the sample may contain copper (<95-percent confidence), but also in lesser amounts than the biotite.

The significance of the presence of copper in biotite and its possible presence in hornblende in sample 246-99B is not

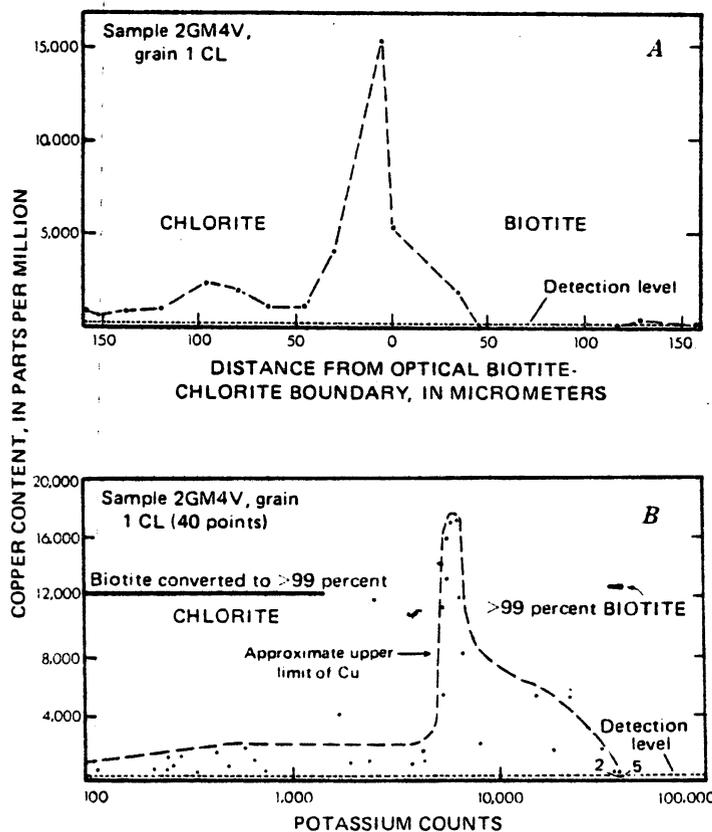


Figure 3.—Distribution of copper in biotite, chlorite, and transitional material. Bars indicate range of potassium (K) counts that designates relatively pure chlorite (<0.1 percent K_2O) and biotite (K counts equal to the average of K counts for biotite grains with no chloritization in the same mount). 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 (Birks, 1963). *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.

clear. The sample is from the most mafic facies (diorite) of the Rattler Granodiorite, a fact that might suggest that copper actually is incorporated in biotite in mafic bodies during crystallization. However, biotite in equally mafic rock (Tortilla Quartz Diorite, table 1) and more mafic rock (diabase, unpub. data) does not contain detectable copper. Thus no trend of increasing copper content of biotite with decreasing silica content of the host rock is established for the rocks of the Ray area.

COPPER-RICH BLEACHED ZONES IN BIOTITE

Some biotite grains in the Granite Mountain Porphyry and older Laramide intrusive rocks have bleached (golden colored) zones oriented parallel to the (001) plane. The zones are sometimes offset along fractures that developed in the biotite prior to consolidation of the magma. Many of these zones are

obvious extensions of chloritized layers, but others do not grade into optically perceivable chlorite at either the middle of the bleached zone or the edge of the grain. Some of the bleached zones contain unexpectedly large amounts of copper (table 3). A copper X-ray image of two such zones is shown in figure 5A. The wider zone is the one analyzed in mount 3GM6G of table 3.

As the small amounts of sulfur in the copper-rich zones indicate (table 3 and fig. 5C), the copper is not present in the form of submicroscopic copper sulfide or sulfate inclusions. In addition, X-ray images of the following elements indicate that they are not present in more than parts per million amounts in the bleached zones: F, Na, P, Cl, Ca, Sc, V, Cr, Co, Ni, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sb, Te, I, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, Pa, and U.

Because of the carbon coating and lack of a suitable analyzing crystal, it could not be determined directly whether carbonates or nitrates account for the copper in the zones. However, the amount of silica in the zones suggests that the copper is not explained by the presence of known carbonates and nitrates, or even known oxides and silicates. Significantly less silica is present in such minerals than in chlorite (0–20 versus 26–27 percent). Therefore, if the zones were simply a mixture of known copper carbonates, nitrates, oxides, silicates, chlorite, and biotite, the amount of silica in the zones having appreciable amounts of copper (analyses G, O, P, Q, R, S, table 3) should be, but is not, measurably less than the amount of silica in chlorite.

It is not within the scope of this report to determine the exact mineralogic composition of the zones, but some speculation is warranted. The zones are assumed to represent incipient chloritization of biotite by fluids that may or may not carry copper, because chlorite occurs at grain edges along many of the zones and copper is concentrated at many optical biotite-chlorite boundaries (figs. 3, 4). However, except for SiO_2 and K_2O , the amounts of individual constituents and structural formulas of the copper-rich zones (analyses B, E, G, H, K, L, O, P, Q, R, S, U, and V, table 3) are not uniformly intermediate between the amounts of individual constituents and structural formulas of the parent biotites (analyses A, D, F, J, N, and T, table 3) and those of chlorite along the same zone or in the same rock sample (analyses C, I, M, and W, table 3). Although an increase in density of the zones relative to chlorite and biotite resulting from replacement of K, Ti, Mg, Fe, and Mn by Cu could account for some of the discrepancies in the nonuniform transition in chemistry between the zones and chlorite and biotite, the density shift is somewhat compensated by the amount of water required in the zones in order to arrive at reasonable totals of the constituents (the qualitative scans eliminate significant contribution to the totals of elements other than H and O). Thus it is apparent that the material in the zones is more than a simple mixture of well-formed chlorite and biotite. In addition, the large amount

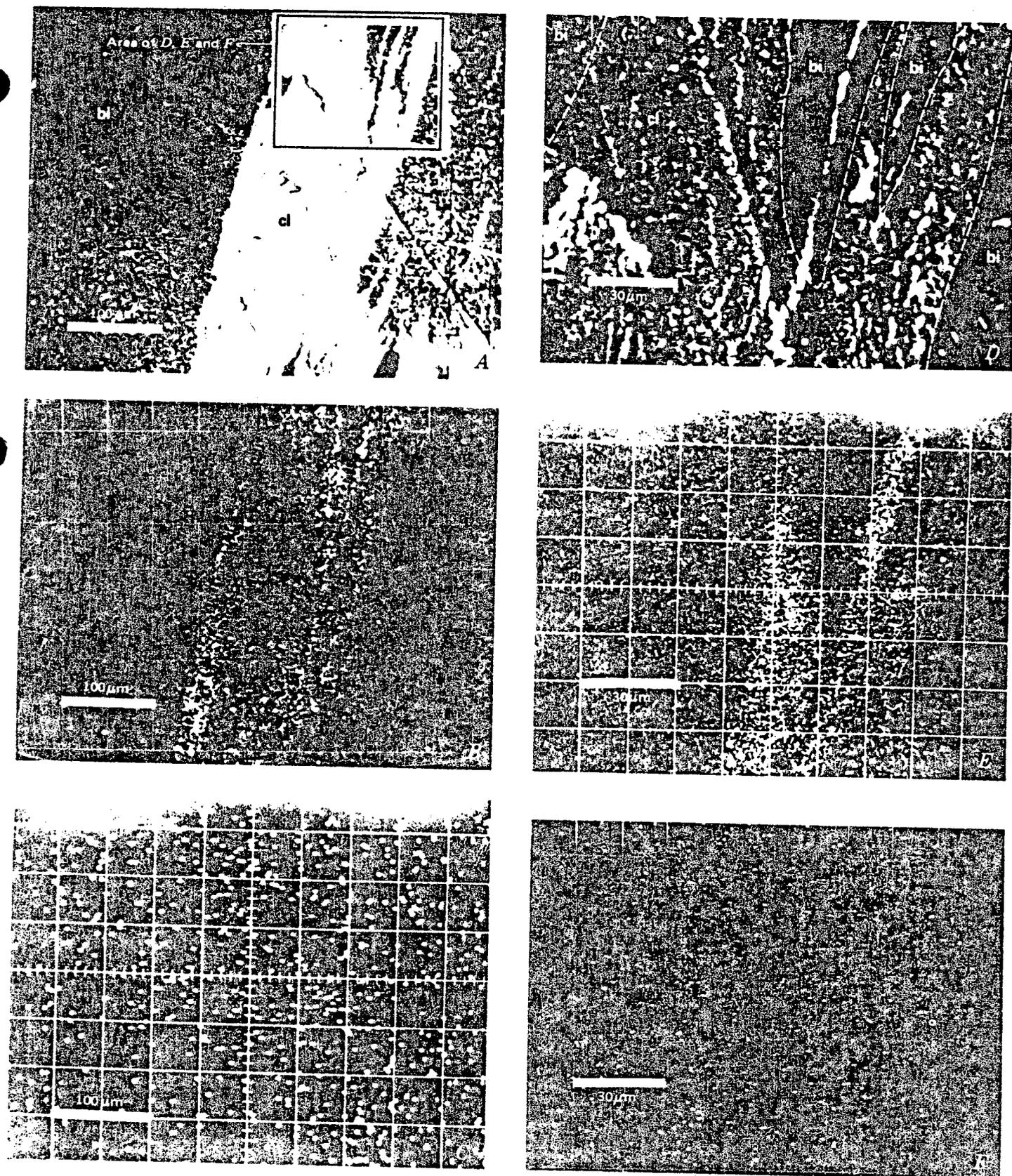


Figure 1. Photographs of electron-beam scans of a biotite-chlorite grain in sample 16-11a. *A*, Scan for sample current of biotite-chlorite grain. The lighter area represents chlorite (cl), and dark areas are biotite (bi). *B*, Scan for copper (same area as *A*), showing its concentration at the mineral boundaries. Exposure time, 2 minutes. *C*, Scan for sulfur (same area as *B*). Note lack of sulfur at the mineral boundaries. Exposure time, 8 minutes. *D*, Scan for sample current of area designated in *A*. *E*, Scan for copper in same area as *D*. Exposure time, 1 minute. *F*, Scan for sulfur in same area as *E*. Exposure time, 4 minutes.

Table 3.—Microprobe analyses and structural formulas for biotite, chlorite,

Mount No.	2GM4V					GM6G
	1			3		
Grain No.						
Area analyzed ...	BIA	BI	CL	BIA	BI	BIA
Mineral	Biotite	Copper-rich zone	Chlorite	Biotite	Copper-rich zone	Biotite
Letter reference in text	A	B	C	D	E	F

Microprobe analysis (percent)

SiO ₂	37.6±0.2	32.7±1.2	27.4±0.3	38.1±0.3	37.2±0.4	36.5±.03
Al ₂ O ₃	15.5±0.1	15.6±0.5	16.8±0.2	14.5±0.1	15.0±0.2	15.6±0.1
FeO ¹	17.4±0.2	19.4±0.7	24.3±0.2	17.6±0.1	17.6±0.1	18.4±0.2
MgO	11.4±0.1	14.4±0.4	16.2±0.1	12.4±0.1	11.5±0.05	11.4±0.1
CaO	(₂)
MnO46±0.01	.32±0.03	.64±0.02	.42±0.02	.42±0.02	.59±0.05
CuO	ND ²	1.1±0.2	.11±0.02	ND	1.4±0.4	ND
TiO ₂	3.2±0.1	.74±0.41	.09±0.010	3.4±0.03	3.5±0.1	2.5±0.1
K ₂ O	9.7±0.1	2.3±0.07	.09±0.018	9.9±0.1	9.0±0.5	9.5±0.2
Cl02±0.004	ND	ND	.03±0.006	.03±0.008	.02±0.006
F77±0.06	.18±0.17	.16±0.03	.86±0.04	.81±0.05	.66±0.06
S01±0.001
Σ	96.1	86.7	85.8	97.2	96.5	95.2
Less O≡Cl+F3	.1	.1	.4	.3	.3
Σ	95.8±0.4	86.6±1.7	85.7±0.4	96.8±0.4	96.2±0.8	94.9±0.5

Structural formulas⁴

Anions per formula	22	22	28	28	22	22	28	22
Si ⁴⁺	5.68	5.35	6.82	5.91	5.71	5.64	7.17	5.60
Al ^{IV}	2.32	2.65	1.18	2.09	2.29	2.36	.83	2.40
Al ^{VI}45	.37	2.65	2.18	.27	.32	2.58	.43
Ti ⁴⁺36	.09	.12	.01	.38	.40	.51	.29
Mg ²⁺	2.57	3.51	4.47	5.21	2.77	2.60	3.31	2.61
Cu ²⁺13	.17	.0216	.20
Fe ²⁺	2.20	2.66	3.38	1.38	2.21	2.23	2.84	2.36
Mn ²⁺06	.04	.06	.12	.05	.05	.07	.08
K ⁺	1.87	.48	.61	.02	1.89	1.74	2.21	1.86

¹ Total Fe calculated as FeO.

² Blanks indicate no analysis was made for the component.

and copper-rich zones in biotite from Granite Mountain Porphyry

GM6G-Continued

3-Continued			4		
Cul	Cu3	CLA Chlorite	BIA Biotite	Cul	Cu3
Copper-rich zone				Copper-rich zone	
G	H	I	J	K	L

Microprobe analysis (percent)-Continued

32.9±2.4	34.9±2.3	26.6±0.4	37.0±0.4	33.4±2.9	36.3±0.7
13.5±0.7	14.3±0.7	17.3±0.2	14.7±0.2	13.5±1.3	14.0±0.3
15.3±0.9	17.0±0.7	24.2±0.2	17.6±0.1	16.2±0.3	17.4±0.4
9.5±1.3	11.3±0.7	16.4±0.1	11.9±0.1	10.6±0.2	11.4±0.5
.....
.46±0.05	.51±0.05	.86±0.03	.56±0.01	.46±0.03	.05±0.028
13.5±0.9	4.6±0.9	.43±0.04	ND	1.0±0.6	5.3±0.8
3.5±0.7	4.8±3.8	.08±0.02	3.8±0.1	3.0±0.6	3.5±0.1
4.6±1.9	7.7±1.9	.09±0.03	9.4±0.1	5.5±0.7	8.1±1.2
ND	ND	ND	.03±0.006	.06±0.03	.04±0.007
.70±0.13	.79±0.17	.09±0.08	.69±0.04	.86±0.14	.73±0.09
.01±0.001	.01±0.001	ND	.02±0.002	.02±0.002	.02±0.002
94.0	95.9	86.1	95.7	84.6	96.8
.4	.33	.4	.3
93.6±3.7	95.6±5.1	86.1±0.5	95.4±0.5	84.2±3.4	96.5±1.8

Structural formulas⁴-Continued

22	28	22	28	28	22	22	28	22	28
5.69 } 8.00	6.80 } 8.00	5.40 } 8.00	6.87 } 8.00	5.74 } 8.00	5.63 } 8.00	5.69 } 8.00	7.24 } 8.00	5.57 } 8.00	7.09 } 8.00
2.31 } 8.00	1.20 } 8.00	2.60 } 8.00	1.13 } 8.00	2.26 } 8.00	2.37 } 8.00	2.31 } 8.00	.76 } 8.00	2.43 } 8.00	.91 } 8.00
.40 } 8.00	2.09 } 8.00	.01 } 8.00	2.19 } 8.00	2.14 } 8.00	.26 } 8.00	.40 } 8.00	2.69 } 8.00	.10 } 8.00	2.31 } 8.00
.38 } 8.00	.54 } 8.00	.56 } 8.00	.71 } 8.00	.01 } 8.00	.43 } 8.00	.38 } 8.00	.49 } 8.00	.40 } 8.00	.51 } 8.00
2.69 } 8.00	2.92 } 8.00	2.61 } 8.00	3.32 } 8.00	5.28 } 8.00	2.70 } 8.00	2.69 } 8.00	3.42 } 8.00	2.61 } 8.00	3.32 } 8.00
.13 } 8.00	5.98 } 8.00	.54 } 8.00	.68 } 8.00	.07 } 8.00 } 8.00	.13 } 8.00	.16 } 8.00	2.61 } 8.00	3.32 } 8.00
2.31 } 8.00	2.65 } 8.00	2.20 } 8.00	2.80 } 8.00	4.37 } 8.00	2.24 } 8.00	2.31 } 8.00	2.94 } 8.00	.61 } 8.00	6.02 } 8.00
.07 } 8.00	.08 } 8.00	.07 } 8.00	.09 } 8.00	.16 } 8.00	.07 } 8.00	.07 } 8.00	.08 } 8.00	2.23 } 8.00	2.84 } 8.00
1.19 } 8.00	1.21 } 8.00	1.52 } 8.00	1.93 } 8.00	.02 } 8.00	1.82 } 8.00	1.19 } 8.00	1.52 } 8.00	.07 } 8.00	.01 } 8.00
.....	1.59 } 8.00	2.02 } 8.00

³ND means component not detected at the following amounts: 0.01 percent CuO, 0.03 percent TiO₂, 0.005 percent S, 0.01 percent Cl, 0.04 percent F.

⁴Structural formula calculated on an anhydrous basis using computer program of Jackson and others (1967). Formulas exclude Ca, S, Cl, and F.

Table 3.—Microprobe analyses and structural formulas for biotite, chlorite,

Mount No.	GM6G-Con.	3GM6G			
Grain No.	4-Con.	1			
Area analyzed	CLA	G	A	C	D
Mineral	Chlorite	Biotite	Copper-rich zone		
Letter reference in text.	M	N	of	P	Q

Microprobe analysis (percent)—Continued

SiO ₂	26.6±0.2	37.4±0.2	31.1±0.9	30.4±0.2	30.8±0.8
Al ₂ O ₃	19.2±0.2	14.9±0.2	14.5±0.1	14.4±0.1	14.1±0.6
FeO ¹	22.5±0.3	18.5±0.2	14.5±0.3	13.9±0.2	13.5±0.6
MgO	16.4±0.2	12.3±0.1	10.3±0.2	9.8±0.1	9.7±0.4
CaO	ND	.34±0.07	.24±0.05	.15±0.03
MnO96±0.07	.50±0.02	.32±0.02	.31±0.02	.28±0.02
CuO01±0.001	ND	12.6±0.6	12.1±0.4	14.4±0.8
TiO ₂16±0.03	3.9±0.1	3.0±0.1	3.0±0.1	3.0±0.1
K ₂ O11±0.03	9.6±0.3	2.2±0.5	1.8±0.2	1.9±0.4
Cl	ND
F16±0.03
S	ND
Σ	85.9	97.1	88.9	86.0	87.8
Less O≡Cl+F1
Σ	85.8±0.5	97.1±0.5	88.9±1.3	86.0±0.6	87.8±1.2

Structural formulas⁴—Continued

Anions per formula	28	22	22	28	22	28	22	28
Si ⁴⁺	5.66	5.58	5.22	6.65	5.25	6.68	5.25	6.68
Al ^{IV}	2.34	2.42	2.78	1.35	2.75	1.32	2.75	1.32
Al ^{VI}	2.48	.21	.09	2.30	.17	2.40	.08	2.28
Ti ⁴⁺03	.44	.38	.48	.39	.50	.38	.49
Mg ²⁺	5.20	2.74	2.58	3.28	2.52	3.21	2.46	3.14
Cu ²⁺	1.60	2.03	1.58	2.01	1.85	2.36
Fe ²⁺	4.01	2.31	2.04	2.59	2.01	2.55	1.92	2.45
Mn ²⁺17	.06	.06	.06	.04	.04	.04	.05
K ⁺03	1.83	.47	.60	.40	.50	.41	.53

¹Total Fe calculated as FeO.

²Blanks indicate no analysis was made for the component.

and copper-rich zones in biotite from Granite Mountain Porphyry -Continued

3GM6G-Continued		GM12			3 CL Chlorite
1-Continued		2			
E	F	BIX	BIA	BIB	W
Copper-rich-zone-Continued		Biotite	Copper-rich zone		
R	S		T	U	V

Microprobe analysis (percent)-Continued

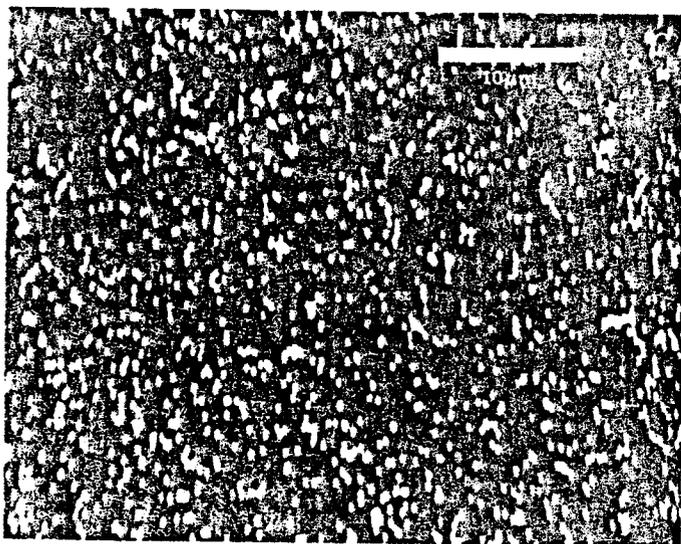
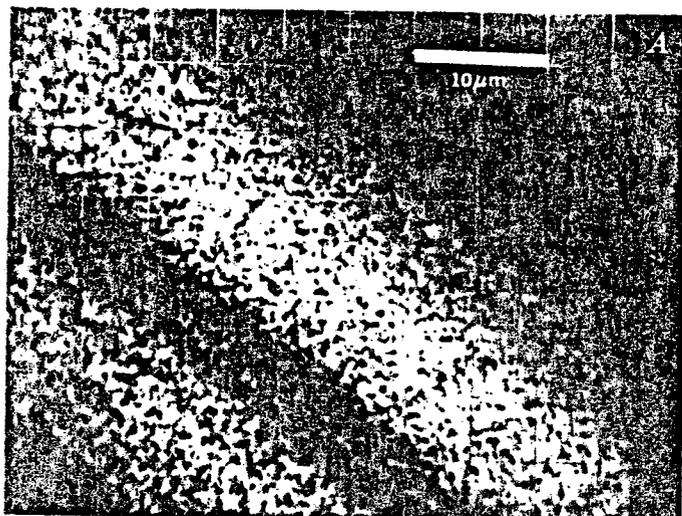
30.7±0.6	31.4±0.7	37.1±0.1	37.0±0.5	37.3±0.8	27.4±0.2
14.6±0.2	15.1±0.2	14.4±0.4	13.5±0.4	13.4±0.3	17.9±0.3
15.1±0.5	14.8±0.3	18.0±0.1	14.9±0.5	14.9±0.3	22.9±0.2
9.8±0.3	10.2±0.3	11.8±0.1	13.1±0.4	13.3±0.4	17.2±0.1
.25±0.24	.17±0.02
.30±0.02	.35±0.04	.69±0.05	.46±0.2	.45±0.03	.93±0.03
15.3±0.7	10.1±1.5	ND	.19±0.04	.19±0.04	.09±0.01
3.1±0.1	3.3±0.1	4.1±0.1	3.2±0.1	3.3±0.1	.05±0.009
2.6±0.1	4.2±0.5	9.4±0.1	7.3±0.2	7.6±0.1	.18±0.03
.....03±0.01	.03±0.02	.01±0.007	ND
.....69±0.05	.90±0.13	.91±0.12	.14±0.02
.....02±0.002	.01±0.001	.01±0.001
91.8	89.6...	96.2	90.6	91.4	86.8
.....3	.4	.4	.1
91.8±1.1	89.6±1.8	95.9±0.5	90.2±0.9	91.0±1.0	86.7±0.4

Structural formulas⁴-Continued

22	28	22	28	22	22	28	22	28	28
5.09	6.48	5.21	6.63	5.63	5.82	7.41	5.82	7.41	5.80
2.86	1.52	2.79	1.37	2.37	2.18	.59	2.18	.59	2.20
.....	2.11	.16	2.39	.20	.32	2.59	.29	2.55	2.27
.39	.49	.41	.52	.47	.38	.48	.39	.49	.01
2.42	3.08	2.52	3.21	2.67	3.07	3.91	3.10	3.94	5.43
1.91	2.44	1.27	1.6102	.03	.02	.03	.01
2.09	2.66	2.05	2.62	2.28	1.96	2.49	1.95	2.48	4.06
.04	.05	.04	.06	.09	.06	.08	.06	.08	.17
.55	.70	.89	1.13	1.82	1.46	1.86	1.51	1.93	.05

³ ND means component not detected at the following amounts: 0.01 percent CuO, 0.03 percent TiO₂, 0.005 percent S, 0.01 percent Cl, 0.04 percent F.

⁴ Structural formula calculated on an anhydrous basis using computer program of Jackson and others (1967). Formulas exclude Ca, S, Cl, and F.



of copper in the transitional material is not easily explained by either substitution or attachment of copper in well-formed chlorite and biotite in view of the relatively low amount of copper in well-formed chlorite and biotite (fig. 3; tables 1 and 2).

Whether the material is partly destroyed biotite, poorly formed chlorite, another well or poorly formed sheet silicate, or a mixture of these cannot be determined from existing data. However, the data do restrict the type or amount of possible sheet silicates that could make up the material in the bleached zones. The silica content of the zones, being less than biotite, indicates that if no chlorite is present in the zones and biotite either is or is not present, the sheet silicates that could make up the zones are septechlorite, clintonite, xanthophyllite, margarite, silica-poor montmorillonite, or vermiculite. The small amount of calcium in the zones (analyses O, P, Q, R, and S, table 3) indicates that of these, margarite, clintonite, and xanthophyllite probably are not present. On the basis of the color of the zones, their refractive index, birefringence, the leachability in acid of copper in biotite-chlorite grains (mentioned earlier), and the number of exchange sites available, vermiculite or montmorillonite seem to be more likely alternatives to septechlorite, if indeed another sheet silicate is present in the zones. Montmorillonite is possibly less likely than vermiculite because smaller amounts of alumina are expected in silica-poor montmorillonite. Alternatively, if chlorite composes part of the zones, the data do not negate the presence of a sheet silicate having more silica than biotite; however, the amount of such a silicate that could be present is limited by the amount of chlorite required to dilute the higher amounts of silica in these minerals to those observed in the zones. Thus if most of the copper were present in a high-silica silicate, the amount required is much more than that required in vermiculite.

The zones often include apatite grains and are wider around them. In addition, the zones commonly contain or are near swarms of suboptical-sized apatite as determined by electron-beam scans of the zones for calcium and for phosphorus (fig. 5B). Thus it is suspected that the bleached zones (which range in thickness from <1 to $20 \mu\text{m}$) extend completely through 3-mm-sized biotite grains and in places are offset along fractures that developed prior to consolidation of the magma because of favorable permeability conditions in the biotite resulting from the deformation and expansion of the grains by the apatite inclusions.

Figure 5. Photographs of electron-beam scans of copper-rich zones in mount sample 3GM6G. A, Scan for copper. Exposure time, 1 minute. B, Scan for phosphorus of same area as A. Exposure time, 1 minute. C, Scan for sulfur of same area as A. Exposure time, 10 minutes.

COMPARISON OF MAJOR-ELEMENT CHEMISTRY OF THE COPPER-RICH AND COPPER-POOR CHLORITES

The presence or absence of copper in chlorite could possibly be attributed to its formation at different times or from different fluids; hence, the resulting chlorites might be differentiated on the basis of chemistry. However, preliminary data indicate that except for the presence of copper, chlorite that contains copper is similar in chemistry to chlorite that does not contain copper (fig. 6). In fact, the composition of chlorite appears dependent in larger part on the composition of the parent biotite than on the copper-depositing characteristics of the altering fluid (fig. 7). Preliminary observations also revealed no optical dissimilarity between copper-bearing and

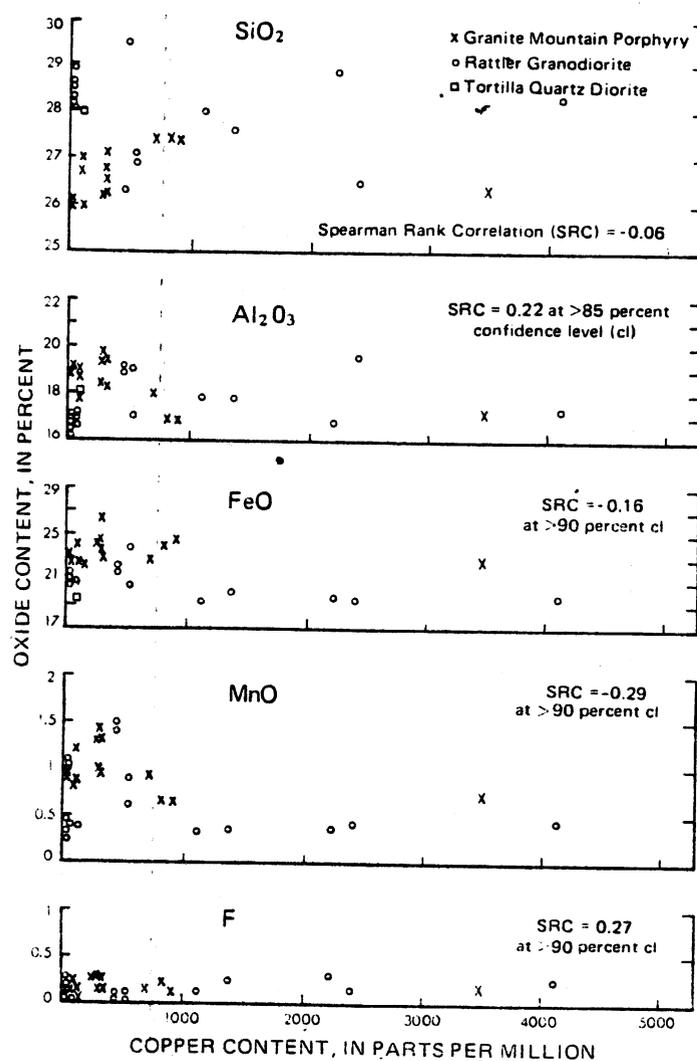


Figure 6.—Graphs showing amounts of representative chemical components in chlorite in relation to amount of copper in chlorite. Some points are offset slightly for plotting purposes. Four additional points (three for Rattler Granodiorite and one for Tortilla Quartz Diorite) plot near the origin of the F versus Cu diagram.

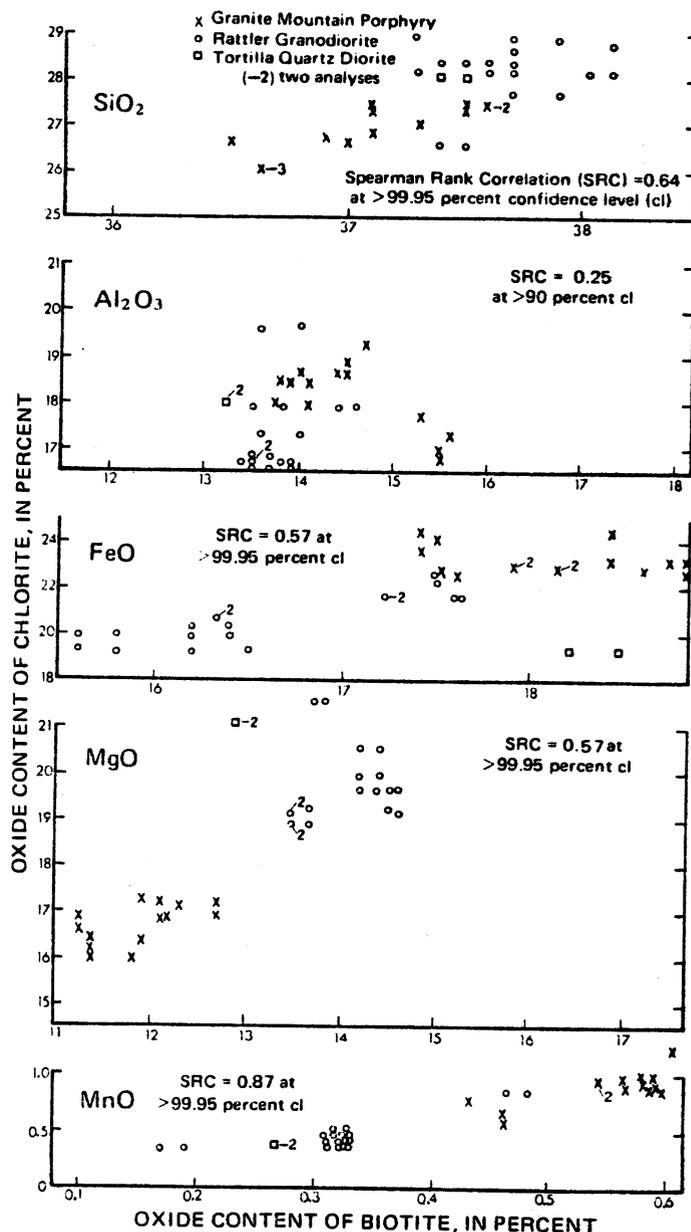


Figure 7.—Graphs showing the amount of oxide in biotite in relation to the amount of oxide in chlorite derived from the biotite. Some points are slightly offset for plotting purposes. The statistics include two biotite-chlorite pairs that plot off the diagrams.

copper-poor chlorite. Thus it could not be established whether chlorite formed in the rocks at two different times from two fluids.

VALUE OF THE COPPER CONTENT OF CHLORITE AS AN INDICATOR OF ORE

The occurrence of copper-bearing chlorite derived from igneous biotite near two ore deposits suggests that the amount of copper in chlorite might serve as a geochemical indicator for

a nearby copper ore deposit. However, copper in chlorite does not seem to show a simple positive relation with the proximity of the sample to a presently recognized deposit (fig. 8). This lack of correlation may result from inadequate data or from the possibility that the copper content of chlorite depends on factors other than, or in addition to, the distance of the chlorite grain from a minable deposit.

Inadequacy in the data is suggested by the extreme variation in the amount of copper in chlorite both between grains in the same probe mount (thin section, 1-in. diam) and within

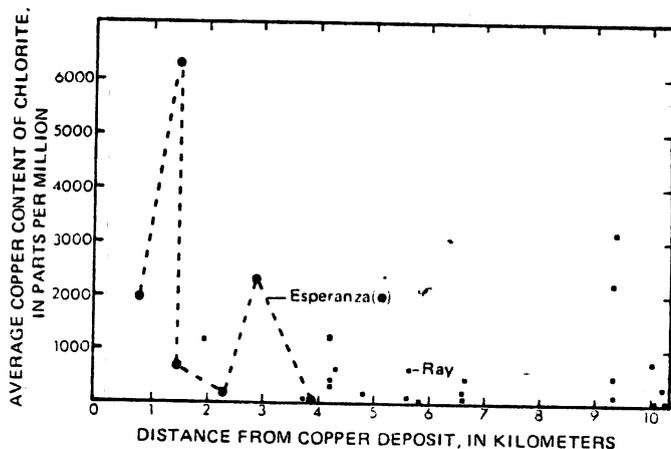


Figure 8.—Plot of average amount of copper in chlorite in a given sample in relation to distance of the sample from the nearest recognized commercial deposit.

individual grains (figs. 3, 4; tables 1, 2). Thus determination of the true average abundance of copper in chlorite in each rock sample is too expensive to refine with microprobe analyses because a prohibitive number of grains must be analyzed in a prohibitive number of mounts. The alternative method of determining the true abundance of copper in chlorite by conventional analyses of separates may also be limited by the various types of bias that are built into mineral separations (magnetic, electrostatic, specific gravity, and optical)—the resulting separation may be 100 percent chlorite, but in view of the irregular distribution of copper in chlorite and of the fact that much copper resides in the more poorly crystallized chlorite, the mineral separate is likely to contain copper in an amount not representative of the average.

These observations do not rule out the potential use of copper abundance in chlorite as a geochemical indicator. If standardized separation techniques are used, it is still possible that the content of either leachable or total copper in mica or chlorite separates may correlate roughly with proximity of the sample to a deposit. Additionally, the copper content of chlorite may be of limited usefulness as a broader indicator of ore; that is, it might point out potential copper-producing provinces. For example, the copper content of chlorite from Sierra Nevada rocks (Dodge, 1973) with no known associated

porphyry-type deposits is much less than that of chlorites reported here. However, this again may reflect mineral separation problems because Dodge analyzed clean mineral separates that probably were relatively free of poorly crystallized chlorite.

Finally, assuming that the true average abundance of copper in chlorite (or an abundance determined by analysis of concentrates separated in a standardized way) could be determined, caution should be used in its application as a geochemical indicator of ore because there is reason to suspect that this abundance could be influenced by factors other than the distance of the sample from a minable copper deposit. These factors include the rate of chloritization, percentage of partial chloritization, number and size of grains chloritized, the number of potential fluid conduits (fractures) per unit volume of rock, the proximity of the chlorite to a fracture, and the concentration of copper in the fluid immediately adjacent to the biotite; the first three factors would control the number of sites suitable for copper capture, and the latter three are measures of the availability of the chlorite to the copper in the supplying fluid.

CONCLUSIONS

Copper occurs in chlorite derived from igneous biotite in Laramide intrusions around two Arizona porphyry copper deposits and, further, is concentrated at the boundary between parent biotite and chlorite. However, the copper content of igneous and hydrothermal biotite near these deposits was found to be much less than that of chlorite and was not detected in most of the grains analyzed. In view of the difficulty in cleaning chlorite from biotite separates, these observations suggest that caution should be used in speculations about what the abundance of copper in biotite derived from bulk-analyzed mineral separates might mean with respect to the genesis or proximity of ore deposits and with respect to the behavior of copper in a differentiating magma. Additionally, because a potentially large part of the copper in a whole-rock sample of "granitic" rock may be in alteration products of biotite and thereby conceivably have had its source outside the analyzed sample, caution should be applied to petrologic and genetic interpretations of whole-rock copper abundance data.

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PORPHYRY SYMPOSIUM



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Porphyry Copper Seminars • Research • Publications

Lecture Notes --- Kenyon Richard 10/30/75

Sampling and Evaluating Porphyry Copper Deposits

The word "evaluating" does not mean "complete feasibility study."

This talk will be concerned mostly with vertical coredrill sampling because the use of that method currently is almost universal. The cases for angled drillholes, underground bulk sampling and channel sampling and for rotary and down-the-hole hammer methods will be discussed a bit as we go along.

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Also, I'll be talking about ore reserve estimation, because I've found most geologists and all engineers have handled that problem very carelessly in recent years. Maybe that's because there have not been so many newly-found ore bodies lately. I worked back in the days when it was easy to find ore, and I had a lot of practice, first, in how to make erroneous ore estimates, and then having to repeat the whole tedious procedure correctly.

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Before a deposit or orebody with drillholes itself can be evaluated, the accuracy of the drillhole samples themselves must be evaluated. The best way to obviate this latter problem, which is a very difficult and uncertain exercise at best if the samples are suspect, is to take accurate samples to begin with. That may seem easy, but it is not.

First, accurate samples are expensive. This is a matter of real constraint, but not if you are dealing with a wildcat situation in which little if anything really is known about the geology of pre-mineral rocks. In that context I am assuming that all you have is a geochem., or a geophysical, or a geological anomaly, or all three, in which essentially all information is projected, or otherwise exists only theoretically, beneath gravel, soil, talus or dense vegetation such as jungle. In these circumstances when pre-mineral rock is encountered and assays are less than, say, .05% Cu (or equivalent additive values in other metals), the accuracy, or representativeness of samples is not of consequence, and imprecise samples are acceptable. As soon, however, as values get into the range of .1 to .2% Cu, good drilling and sampling techniques with high core recovery should be undertaken.

Some of the statements herein may seem elementary or self-evident. Yet, even with the modern drilling equipment that is available, the carelessness of many current sampling procedures is remarkable. This is true even in the U.S. where good equipment and sampling techniques for porphyry copper deposits were developed, but carelessness here is prevalent, I suspect. I recently saw what I presume is a currently standard drilling contract. I was appalled. It was written by a contractor for himself. If the contractee eventually gets accurate samples it will only be because the drillers actually are conscientious. The contractee has no real control over whether the core samples are good or poor. The drilling cost in that particular contract was high. But that didn't bother me. I personally don't care, really, whether a core sample costs \$5 or \$50/ft.-----if it is representative. (I have participated----usually in a nervewracking way----in projects where large expenditures in checking drill-ore sample accuracy were necessary before total financing could be finalized. That is why I'm very particular about sample accuracy.)

This sloppiness in drillcore sampling prevails, I think, because so many prospects are drilled and abandoned without finding ore, or else the material found is so marginal in

grade that things are put on the shelf. In these cases it may take years or decades to discover that all samples were systematically low, or high, due to low core recovery or some other careless procedure.

The net result is that there are many projects which never reach the stage of ore reserve calculation or financing at which time a glaring spotlight can be focused on sample accuracy. Thus, a great amount of drilling is done in which not much thought is given to sample accuracy. Geologists, contractors, foremen, drillers-----everyone-----has grown careless in recent years.

Sampling of any kind of course means that one or many small samples are taken in a manner that they are supposed to represent the whole mass. For our purposes perfection depends (1) on grain size and/or the textures of the valuable minerals, the hardness or softness of the rock, and the frequency of changes in these physical characteristics, and (2) on the number of samples. This degree of perfection could be derived by the mathematical theory of sampling---you can, and should, look that up in the older handbooks of metallurgists. You'll be surprised as to how high a proportion of the sample is required for an accurate sample of the mass as the grain and fragment sizes become larger---but in exploration work we cannot expect to come up with an ore body which is "mathematically perfectly measured", to the same high degree that a metallurgist may require in his milling control sampling.

For our exploration sampling purposes we should attempt to approach mathematical precision. But the matter of how close we get to precision is, unfortunately, conditioned by costs and the availability of money.

The people who put up or control the money supply for exploration usually are tight-fisted because exploration is a lottery, whether we, as explorationists, admit it publicly or not, and they are more-or-less aware of the gambling risks of finding an ore body. They usually are not aware, however, of the really serious risks of ending up with an ore body for which the core samples are under suspicion, by the financiers and their advisors, of being inaccurate.

The geologist in charge of any part, or the whole, of an exploration program must continually push for money. If he really believes in his program he often must badger the money people, to the point of almost risking his own job. This is all a matter of personal judgment tempered by experience and just plain hunch of the geologist.

I think the first porphyry copper ore bodies were "blacked out", or whatever you want to call it, by driving adits, crosscuts and raises on 200' to 400' centers then milling the bulk material and/or channel sampling the walls of the workings. This was done at Ely and Bingham Canyon about the turn of the century. Around 1906 churn drilling at Ray was tried, successfully, because some really smart engineers happened to be doing the work, and because the drillholes were not very deep. On that first job, underground workings and raises were driven on some of the drillholes. The comparison was an almost perfect check. Shortly thereafter diamond drilling was attempted in many districts with questionable degrees of success. Both were used during the 20s, 30s and 40s. Most individuals favored the churn drill because the 'bulk' of each sample had a sort of magic connotation of automatic accuracy. The diamond drill however was cheaper and more mobile. Arguments over which equipment was best were heated during those years. Actually, the arguments should have revolved around which method was least worse, particularly as drillholes became deeper and got into the ground water. Both were subject to serious systematic errors. Principally, the churn drill sample was subject to salting by caving from the wall of the drillhole above the sample interval. This became worse below the water table. With only the rigid core barrel and screw-feed machines available, diamond core recovery usually averaged only 10 to 30%, and the accuracy of recovered diamond drill sludge samples was always dubious. The application of formulae for combining diamond core and sludge samples, such as the famous but erroneous "Longyear Formula", was another cause of many arguments. During the 40s improvements in diamond drilling equipment such as hydraulic feed, wireline, mud circulation, truck mounting and swivel barrels improved the core recovery and lowered costs to the extent that churn drills were phased out in the 40s and 50s. Incidentally, the swivel, or non-rotating or double tube barrel, not wireline, was the single most

important piece of new equipment ever developed for sampling porphyry copper deposits because it alone improved core recovery from, say 20 to 90%.

The foregoing brief comments have been made because in former decades the reliability of drillhole samples, individually and collectively, and of various types, often was subject to serious doubts and had major influence on the dealing and financing of ore bodies. Occasionally now-a-days, one is confronted with old drillhole samples acquired with questionable equipment and techniques, and, as mentioned before, even today questionable samples of ore bodies are being taken with poor equipment and poor sample handling methods.

If a person is confronted with a number of drillholes and their assays representing thousands or even only hundreds of samples, the matter of sample accuracy should be examined critically whether the samples are new ones or very old. The problems usually get worse with age. In any case the matter can never be ignored----and you cannot just throw everything away and say "Redrill every hole!" If you have a bunch of assays you should be stuck with demonstrating they are accurate, or, if inaccurate, how inaccurate.

Engineers have 4 irritating methods of getting around this problem.

(1) They begin a report with the statement "If it is assumed that the samples are correct"-----then they go through a 100-page report about everything else including discounted cash flow to the year 2000. This gets the engineer off the hook because by the time the reader has tried to digest the details of the report he has forgotten that opening sentence.

(2) Another engineering stunt is when an ore reserve estimate is made in which a number of safety factors, sometimes hidden, are introduced. This results in the so-called "conservative" report in which the word "conservative" is supposed to be synonymous with "virtue." Actually, when I hear or read the word "conservative" I automatically assume that something is wrong. Most likely the ore body is bigger and better than the bottom line numbers would indicate. But sometimes, of course, the word "conservative" means that something is faked.

On the other hand, I know of several cases where actual ore bodies were "safety factored" out of existence. These situations mostly were due to "misguided conservatism" not dishonesty, although some of them may have been motivated by fear of loss of job or promotion.

(3) Another approach is to decide to "check" the questionable samples either with new drillholes or with underground workings which provide magical "bulk" samples. Sometimes either or both of these methods really is advisable, as will be described later on. However, sometimes it is done because the fallacious idea seems to have been accepted by many that all drillhole samples always are a bit low, and that a bunch of bulk samples automatically will raise a potential ore body from the "marginal" into the "profitable" category. This alone is not really a valid concept, but I know of several instances where large sums of money were wasted with this idea in the back of peoples' minds.

(4) Another ploy is that underground sampling sometimes is undertaken only as a delaying tactic in which a relatively small amount of money is spent while say, one financial group is trying to raise money for a bigger part of the total deal. In other words, this work and expense may be justifiable in a financial sense, but not really necessary in a technical sense.

Before any program of "checking" old drillhole samples by new drilling or underground work is undertaken, a detective-like search should be made (1) for all old correspondence and periodic daily or monthly reports such as those by drillers, by supervisors, by geologists, by metallurgists, etc., and (2) for all possible stored material such as core, crushed rejects, or assay pulps. By analysing the old written material and by re-assaying and re-studying the stored material in light of modern appreciations of mineralogy and other geological features, it often can be determined that certain systematic errors can be quantified to the extent that "check drilling" or whatever is either unnecessary or at least needs to be done only to a limited degree. For example, a statistical study of samples taken above and below all points where casing was set in all drillholes, both ore and waste, may provide factors by which all assays within certain areas, or drillhole

sequences, or depths can be validly corrected up or down. Or, a study of the texture and mineralogy of the core or underground workings may lead to the valid conclusion that core recovery of only 40 or 50% really does give assays representative of the rock mass. By texture, I'm referring to hard and soft minerals which occur selectively on seams or in matrix.

You may feel that the foregoing remarks only apply to drilling done decades ago when techniques really were bad. But I know of several instances, and I suspect others, where recent and on-going drilling programs are of such a nature that detective work like that mentioned above will have to be done by someone in 1, 5, 10 or 20 years.

Equipment other than modern diamond drills can be used for sampling under certain conditions. For example, if there is reason to suspect the presence of an alteration zone beneath generally flat-lying and, hopefully, thin post-mineral rocks, a number of types of low-cost air or mud rotary equipment can produce a few feet of chips of bedrock for geological study and assay. These samples can be likened to geochem. samples, and accuracy is not a requirement. In fact, this technique is quite valuable in determining the best locations later to drill deep holes with correct coring procedures.

I understand that some consider that the cuttings collected from low-cost, air rotary, or reverse circulation systems, or particularly, down-the-hole hammer drills provide representative samples. I have had but little experience with the more modern types of these rigs, but I wonder if the same problems of salting by caving as with the old churn drills would occur, particularly in deeper drillholes or below the water table.

For momentary analysis of a drilling program let's assume that the following 11 optimum conditions obtain:

(1) The first half-dozen or so drillholes indicate that you might be dealing with an ore body.

(2) Road building is not a serious cost.

(3) The drills are truck-mounted, and only vertical holes will be drilled.

(4) The diamond drills have hydraulic feed with sensitive controls.

(5) The drills will chuck NX or larger core sizes. (The larger the core diameter the better the core recovery.)

(6) Good drilling mud with conditioners and additives is available.

(7) Mud circulation is used continually and mud pumps are adequate for mixing and circulating.

(8) Individuals, whether drillers or foreman, experienced in handling mud are always around to check and change the character of the mud according to rock conditions.

(9) A core-run is always stopped whenever the core barrel is blocked, even if only a few inches of hole progress has been made. There should never be an attempt to core to an even interval such as five feet or two meters for every run. That practice will lead to "grinding" and low core recovery.

(10) Never permit a contractor, foreman or driller to get bonuses for footage of hole drilled. Ideally, they should get a bonus for high core recovery (Say, over 90%) and a penalty for low recovery (Say, less than 70%).

(11) Have your own sampler on each rig each shift. His job is to check the removal of the core from the barrel, and place it properly in order in the core carrying boxes, and to measure and mark each run. He should also check the driller's measurement of rods and "stick-up", keeping precise record of drillhole progress. And he should keep written records of the driller's general activities, problems of drilling, mud control, etc. Do not let the driller or contractor handle these matters for you.

If the foregoing 11 procedures all are used, you will have highly representative samples of almost any kind of rock penetrated. Beyond that point, however, there are opportunities for errors to be introduced in sample handling after the core is removed from the core barrel.

Core splitting with a spring wedge and hammer with half being saved and half sent for crushing and assaying is a common but somewhat controversial procedure. Core is an excellent sample because it is round----that is, symmetrical, in contrast, for example, to a rough-walled channel sample which is unsymmetrical and therefore never really accurate. Wedge-splitting spoils the symmetry of the core, but usually the core half needs to be saved and re-logged by various geologists, and for bench tests by metallurgists. I have checked assayed both halves of split-core for many core runs in ordinary ore and have found the assays of the two halves of short runs diverge as much as 25 to 50% from their average. The error tends to be compensating over long footages, however; and for that reason it is fairly acceptable. Still, the hammer blow tends to send fragments flying, and the sampler unconsciously will put the shiny sulphide pieces in the sack for assay, thus producing a systematic error. The best way to split core is to cut it with a diamond saw. This preserves the sample's symmetry, and it also permits much better geological core-logging. But it is slow and somewhat costly, so it is rarely done, though I advise it.

Sometimes, a small piece of core is saved out of each core run for inspection by future geologists, and the entire remainder is crushed for assay. In effect this reduces core recovery by some 5% and so introduces a potential, small systematic error. Generally, though, it is a good practice.

Another method is to crush the entire core for assay. This is good because it retains the integrity of the core sample. Sometimes it is poor, however, because it eliminates re-inspection of the core. In this, as in all cases, a Jones-splitter portion of the crushed (-1/4") material is retained. A small portion of this crushed "reject" always should be glued in strips on a narrow board. The assay and depth is plotted beside each sample. (See example). These are variously termed "core boards", "sludge boards", or "sand boards." Actually, this kind of record of the samples of a hole drilled by any method is of great advantage in geological interpretation because it permits fast recognition of subtle mineralogical changes in one drillhole or among several drillholes. These differences or similarities in alteration, rock types, etc. can otherwise be lost or unrecognized in the detailed written descriptions of core. Also, it is a hell of a job to haul out 200 or 300 boxes of core for geological review of some uncertainties----or, to show a visiting consultant. Also, the retained crushed core fragments can be briquetted and polished for detailed, later geologic study. That sometimes becomes desirable in metallurgical as well as geological study.

All split core, crushed rejects and ground pulps should be carefully labelled and permanently stored. Often in the financing of ore bodies these stored materials become highly important for check work. Even if no ore body is found, remember that over the past 75 years marginal waste has become ore with regularity about every 10 years.

If oxidized Cu minerals or chalcocite with pyrite are present, materials should be stored in tight containers because additional oxidation can take place within a matter of days.

Until now I have been talking about the accuracy of individual samples of drillholes. To summarize that aspect, careless collection of individual samples is permissible if you don't penetrate any ore or near-ore-grade material on any single project. If, however, results indicate you might be dealing with an ore body, accurate individual samples should be obtained pretty much regardless of cost. If you cannot get enough money to insure accurate samples, you should at least get yourself on record that the samples might be systematically inaccurate. Regardless of your own position in the order of responsibility at that time, if it later develops that the samples within and around an ore body actually were systematically inaccurate or even suspect, trouble will be explosive and the fall-out can hit anyone-----but most often the geologist.

When results indicate there might be an ore body around somewhere----the spacing of drillholes assumes more and more importance.

In considering the sampling of an ore body in its entirety, accuracy is a function of "measurement" or, in other words, hole-spacing. In turn, this is another function of money-availability. The depth of drillholes also is involved here as a function just like hole-spacing. I don't have the time to go into all the variables in that equation, except, to advise you to take what comfort you can in the fact that, when everything is finished, all drillholes will turn out to have been either too deep or too shallow.

Any new drilling project whether it is in a new, untested region or in an untested or incompletely tested part of an old district has, of course, some kind of target area defined. This area may be either vague or sharp. And it is to be presumed, hopefully, that it has been defined as well as practicable by regional and detailed geologic mapping, by geochem, or geophysical surveys, by photogeology, or by whatever combinations. Actually, if the prospect is an obviously good one, some of those surveys may not be finished or even begun when the drills arrive. You then have to spot drill locations sooner than you might like.

Anyway, in the more normal beginning situation, anywhere from 2 to a dozen or more drillholes may be planned. Whatever the number, it is assumed that money is authorized for that number of drillholes. Never ask for money for only a single drillhole, because the results from it may be a fluke.

Although the locations of the first few drillholes can be planned, there should be flexibility. Particularly if he is isolated, the geologist running the project in the field should be allowed to change drillhole locations according to his interpretations of the significance of the core as he sees it from day to day. This means that the geologist in the field should have had sufficient experience that the various supervisors on up the line of authority do have confidence in the field man's ability to recognize something important as soon as it shows up in the core, and adjust drillhole locations accordingly.

This all implies that early drillholes are usually located in a random pattern, and that it should be expected that each successive drillhole should be spotted with a "take-your-best-shot" attitude. Don't be averse to the abandonment of some access roads and building new ones.

When the money for the original project of drilling is gone it is to be expected that the program will be suspended or terminated----unless, of course, a few of the drillholes are in ore-grade material. In that happy event, among a variety of speculative considerations, one topic which usually crops up and is given unnecessary importance is, "What drill grid and drillhole spacing should we use and how should it be oriented?" There is a tendency for some individuals in authority to impose at that time in the drilling program a rigid, square pattern of 200', or of 100 meters, or 400', or 75', or rectangles or triangles. Actually, the matter is rather unimportant once it is realized that no single pattern and spacing is best for all porphyry ore bodies, and different parts of the same ore body should have differing drillhole spacings. Many ore bodies have been adequately "measured" by completely random drillhole positioning. I rather favor that technique. But my friend Courtright says something like this, "Use some kind of grid as long as there is no reason not to, but be prepared easily to depart from the grid when special circumstances are recognized." My only argument with him is that once you start with a grid it seems difficult to let go.

Remember, if it begins to seem that you may have an ore body you immediately have two somewhat divergent but simultaneous objectives: They are Exploration and Ore Body Measurement. In the exploration sense you step drillholes outward in wide jumps, or drill some holes extra deep to get some idea of ore body limits. At the same time you should be drilling closer-spaced measurement drillholes. The latter are needed to demonstrate that the first few ore-grade holes are not flukes and to keep up the availability of money. If the ore-grade material is low in tenor or deep, you should not monkey around with very many wide-spaced or deep exploration-type drillholes looking for the limits because you might get too many waste holes too fast. In that case the money supply might get stopped.

Let's assume that we are both exploring and measuring a low-grade deposit. We should be trying to do two things: First, to get some idea of the total tonnage and overall average grade and, second, to determine more precisely the average grade of those small ore production units which will be mined first.

In the first consideration remember there is no such thing as "average" ore because an ore body varies mineralogically and, therefore, probably metallurgically, from place to place. Next, keep in mind that for any ore outside of about 200 million tons, knowledge of the precise grade and tonnage is not really necessary. Further, in a fairly large open pit ore body, production grade and operating waste/ore ratios can be closely controlled

day-by-day and planned ahead for, say 2 or 3 months by blast hole sampling. This cannot be done for a cave-mine ore body; or for a relatively small open pit ore body; so, for these you theoretically need more measurement drillhole assays per unit per volume of ore ----that is, closer-spaced drillholes. The difficulty here lies in the fact that it sometimes requires a good deal of drillhole data before you have an idea how deep your open pit mine will reach, or how shallow your cave-mine can reach. So, as drilling progresses one often does not know exactly what spacing is best in which parts of the ore body.

Toquepala was "measured" for the 1st 10 yrs. and almost measured for the next 10 or 20 yrs. I believe that was the first time that much pre-production drilling had ever been done. As I recall, about 15 yrs. after production started, a program of 100 or more drillholes within the pit were planned. That information was not needed before the first production. I understand La Caridad in Sonora is almost entirely measured; and, considering its huge pre-production investment, \$620 mil., Cuajone surely must be measured for 30 or 40 yrs. of production.

In most large mines interior drilling has been undertaken within a year or two after first ore production----Pima, Sierrita, Mission. At most mines both measurement and exploration programs have been conducted off and on over many years. That has been proper.

At a few mines, however, exploration drilling was begun promptly after production start-up and continued for years, along with substantial increases in mill capacity, and a daily scramble for ore in the mine. Those cases were poor original management. At a few large old mines, essentially no drilling was done for decades after production started. Then, massive programs of exploration were begun and continued for years. Shafts, plants and townsites were moved. Some of those cases were due to faulty original managements, although partly valid excuses existed.

Above 200 million tons of the first and best grade ore to be mined, the average grade and total tonnage figures have usefulness only in determining the size of the plant which should be built. It is almost axiomatic, however, that the bigger the plant the bigger the profit per ton of ore. So, the availability of capital really is the factor which ultimately puts a top limit on plant size. It's nice to brag about having 800 million tons of ore, but what really is important is how carefully has that highest grade, 200-million-ton-best-portion of the ore body been measured by drillholes?

This brings us to the matter of measuring the smaller production units of an ore body. As a crude rule of thumb, about the smallest tonnage for which exploration drillhole samples alone should be used to provide grade predictions is a 3-month's ore supply. Within this parameter there are about 8 considerations.

(1) The grade of the first 3 to 6 months of ore production should be particularly well-sampled----that is, close-spaced drillholes.

(2) Predictions of average ore grade should be quite accurate in yearly ore-production units for the first 5 years---or, until cash flow returns the invested capital. That is important.

(3) Beyond that time the estimate of average grade should be reasonably accurate for each 5-year production unit.

(4) The edges of an ore body should be better-defined as to position, tenor and shape than the rest of the ore body. For example, in open pit mines the waste/ore ratios for thin, low-grade edges of the ore body can become very high. For cave mines the costs of extraction workings are so high that the positions of ore body edges, whether gradational or sharp, should be known pretty closely.

(5) The uniformity or spottyness of the distribution of values in an ore body, or within portions of it, has a direct bearing on drillhole spacing. I cannot give you any good guidelines for drillhole spacing in this regard. It is mostly a matter of geological hunch or experience. I know of one small open pit ore body that was drilled on 75' centers and even that spacing proved to be too wide. There is one large ore body that was drilled on 50' centers. That was ridiculous. Many years ago I saw a map of Bingham Canyon and it seemed to me that tenor was so uniform that 600' spacing would have been close enough. And then there is Chuquicamata which doesn't need any drillholes. At least, when I visited

there in '61 they had mined out about 80% of their drillholes and they were not even taking control samples in the pit. However, many holes have been drilled there since '61.

As a rough guide in working with hole-spacing and spottyness of ore distribution, consider that each 5' drillhole assay-interval has mathematical influence on 500 tons at 100' spacing; at 500' spacing, 25,000 tons are influenced by each assay.

(6) Usually different rock units within an ore body contain differing average values. Thus, structures are important, such as the positions and displacements of post-mineral faults, the shapes of early- and late, pre-mineral intrusives, the shapes of post mineral intrusives, the degree of mineralization control by layered volcanics and sedimentary rocks, and the positions and sizes of breccia pipes. Each of these units may require its own drillhole spacing----if that can be arranged.

(7) Exploration samples should contribute some information (not measurement) on the character of mineralization beneath or outside any easily foreseeable open pit or underground mining.

(8) Often the locations of drillholes is conditioned by unusually high costs of road building where there is steep topography, cliffs, and/or dense jungle. These conditions can sometimes be obviated by drilling angled holes, even nearly flat ones. I still like the vertical drillholes if the extra money can be arranged.

This matter of angled drillholes requires a little special attention. Actually, it is possible to "measure" with fair accuracy an ore body which has been perforated with drillholes angled like jackstraws. But the calculations and geometry are awkward to handle, whether it is done by sections, plan maps and planimeter, or by computer. Drillholes in erratic directions result in too many assays in some blocks of ore and too few in other blocks. In my opinion a good deal of extra money oftentimes can be well-spent in extra drill roads so that vertical drillholes can be used.

There are situations in which a few angled drillholes actually are necessary. These usually involve steep, sharp structural contacts representing distinctive interfaces in values, such as thick pre- or intra-mineral dikes, breccia pipe margins, irregular intra-mineral intrusives, or steep, layered volcanics or sedimentary units, post-mineral faults or steep, thick, close-spaced veins.

Structural conditions which do not require angled drillholes (but where many misguided individuals automatically believe they are necessary) are: (1) very close-spaced, parallel veinlets whether high- or low-angled; (2) low-angle beds or thick ore lenses. The common idea is that through-going structural blocks or zones should be penetrated by drillholes normal to the structure. I do not know why this idea is prevalent----but it certainly is. Possibly it is because the geometry on a section view looks good to amateurs, engineers and even to many geologists who should know better. This is fallacious, except as noted above where sharp contacts and interfaces need to be located precisely, and with another exception where thick lenses of ore or waste have dips of, say, 70° to vertical and are separated by thick lenses of waste.

The real reason for drilling vertical drillholes if at all possible is that core recovery is appreciably higher, as an average. That is important.

In the following I will be concerned only with some of those procedures of ore reserve calculation which either I approve of or dislike.

The basic principal of ore reserve estimation is that the assay for, say, each 5' of drillcore is applied to a volume extending about halfway to surrounding drillholes. This we can call "an area of influence" or "a unit volume" for each assay. This is only a mathematical assumption. We know this is, in a sense, incorrect because the rock really does not maintain precisely the same Cu content in a thin layer extending horizontally for any distance at all. The assumption approaches reality, however when we compare by averaging the assays of many unit volumes, or when we decrease the size of each unit volume by spacing drillholes, with their columns of assays, closer together.

These unit volumes are usually handled geometrically on a stack of plan maps with each map showing the various unit assay-areas of a single mining bench.

If only the total tonnage and its average grade is sought, the data can be compiled on a single map. In a foregoing section I gave some reasons why the results of such a calculation are often not really important. Further, it is pointed out that this geometrical exercise can be classed as "simple" for another reason. Namely, it usually is unrelated to a mining method. Ore reserve estimates are really meaningless if they are not geometrically tied to mining systems. Unfortunately this kind of an estimate; that is, one unrelated to a mining system, provides a mass of rock floating around without anyone specifying what parts of it can be mined. What really irritates me is that it is commonly termed "geological ore." In reality it is usually the work of some mining engineer who doesn't want to stick his neck out by outlining exactly where, how and when each part of the ore body is going to be mined.

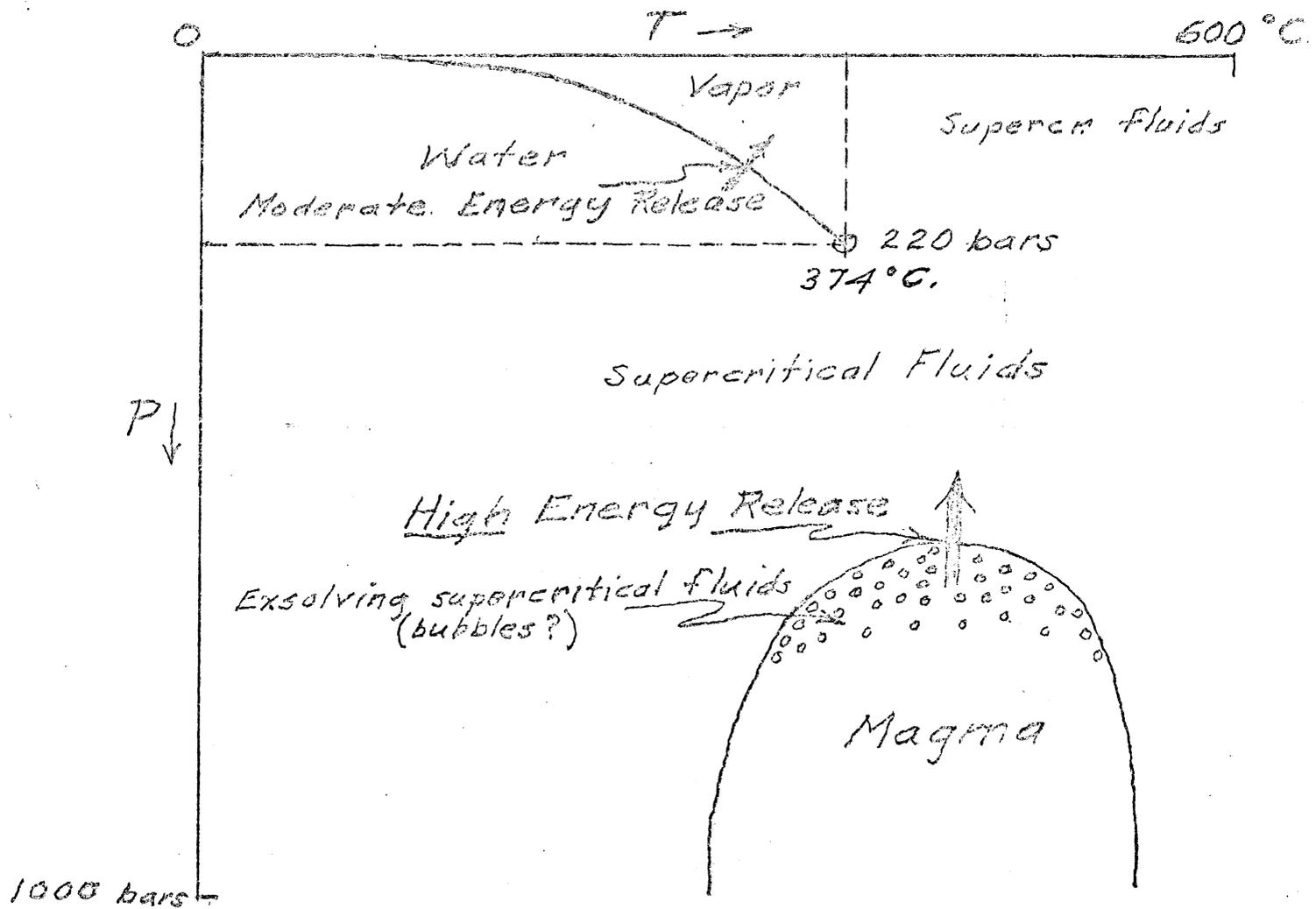
The shapes of each area of assay-influence, or polygon, on each predicted mining bench, can be adjusted in shape to fit the projections of geologic structures where these have a sharp difference in average assay from one side of the structural plane to the other. For example: A column of assays in a drillhole in a breccia pipe may average, say 1.5% Cu whereas surrounding rock averages .5% Cu. If the edge of the pipe can be properly projected to a position on a bench plan that is 50' from a low-grade drillhole and 150' from the high-grade drillhole in the breccia pipe, the polygons are adjusted in shape to match the contact so that the volume influence of higher assays extends, in a mathematical sense, 150' to the contact, and the assay-influence of the low-grade material only extends 50'. This construction of adjusted polygons is accomplished by compiling detailed sets of geologic structure sections through the ore body and plotting all important contacts on each polygon bench plan.

Often pits can be designed (1) for various pit slopes, (2) approximately for different grade cutoffs and (3) for different production intervals such as the shape of the pit at the end of pre-production stripping, the end of the 1st yrs' production, the 5th year, etc. All of these theoretical pit shapes can be plotted on the bench plans and the grade-polygons adjusted accordingly. If the old fashioned system is used, each adjusted polygon on each bench plan is measured by planimeter and the various assay-polygons are subtotaled and totaled by weighted averaging. This can give assay averages and waste/ore ratios for production time-tonnage units ranging from 3 months to 10 yrs. or whatever. All it takes is many thousands of man hours of work.

All of this work can be handled much more rapidly and with the solving of more variables by computers. All that requires is hundreds of man hours while the engineers, geologists and programmers are trying to understand each other and get the bugs out of the programs.

In fairly recent years I've heard of computer programs called something like trend surface analyses. I think they involve a mathematical theory whereby every assay in an ore body has some influence on all assays. As you can realize, I do not really understand it and am therefore leary. I was told recently, however, that programming is back to the basic principles, which I term the adjusted polygon system. The modern computer programmers no doubt have much more elegant terms.

A few years ago some papers about computer programming appeared which demonstrated that in the case of a number of large porphyry ore bodies it could be proved that average grade could have been derived by drilling only a small fraction of the number of holes that were actually drilled. If you have understood me this far, you will appreciate that that idea is ridiculous, but it cheered me up greatly. I could envision the day when, with some further program refinements, we could just plug into a computer some data about a theoretical ore body somewhere and then start mining without putting down any drillholes anywhere.



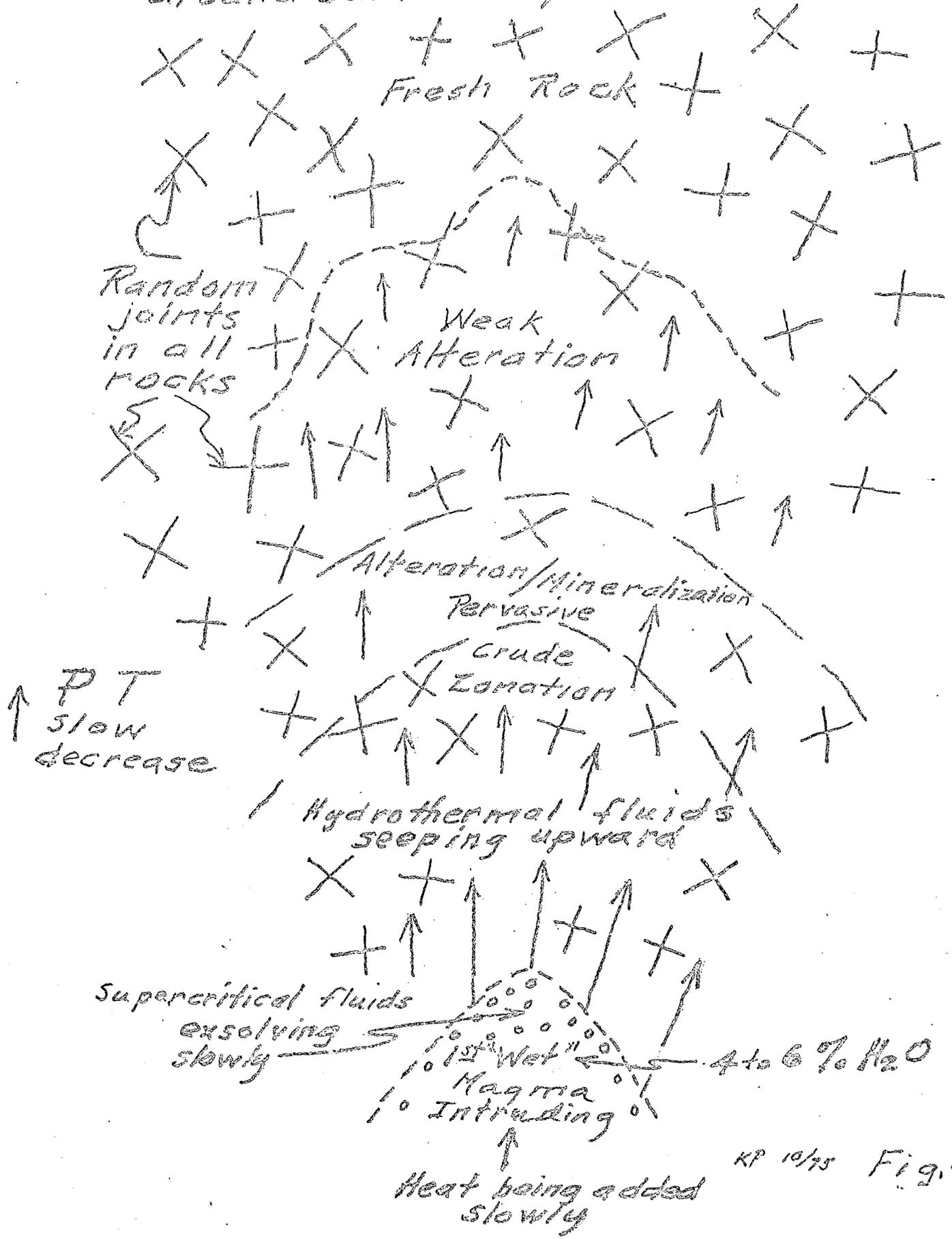
High energy released by exsolution of supercritical fluids from magma if rate of PT drop is rapid. This can produce detonations and diatremes.

When PT crosses water/vapor line, sufficient energy released to brecciate shallow rocks.

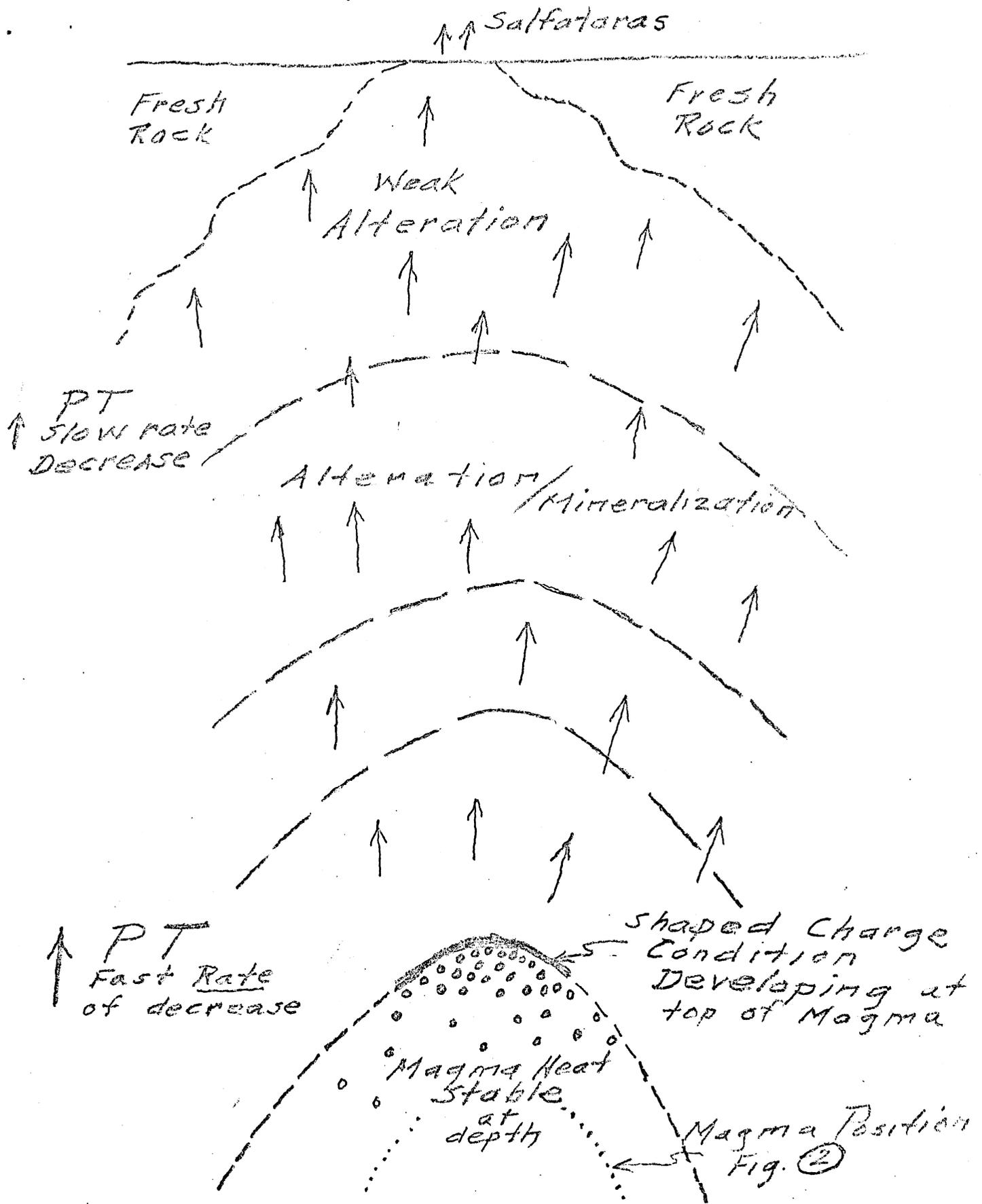
KR 10/15

Fig. ①

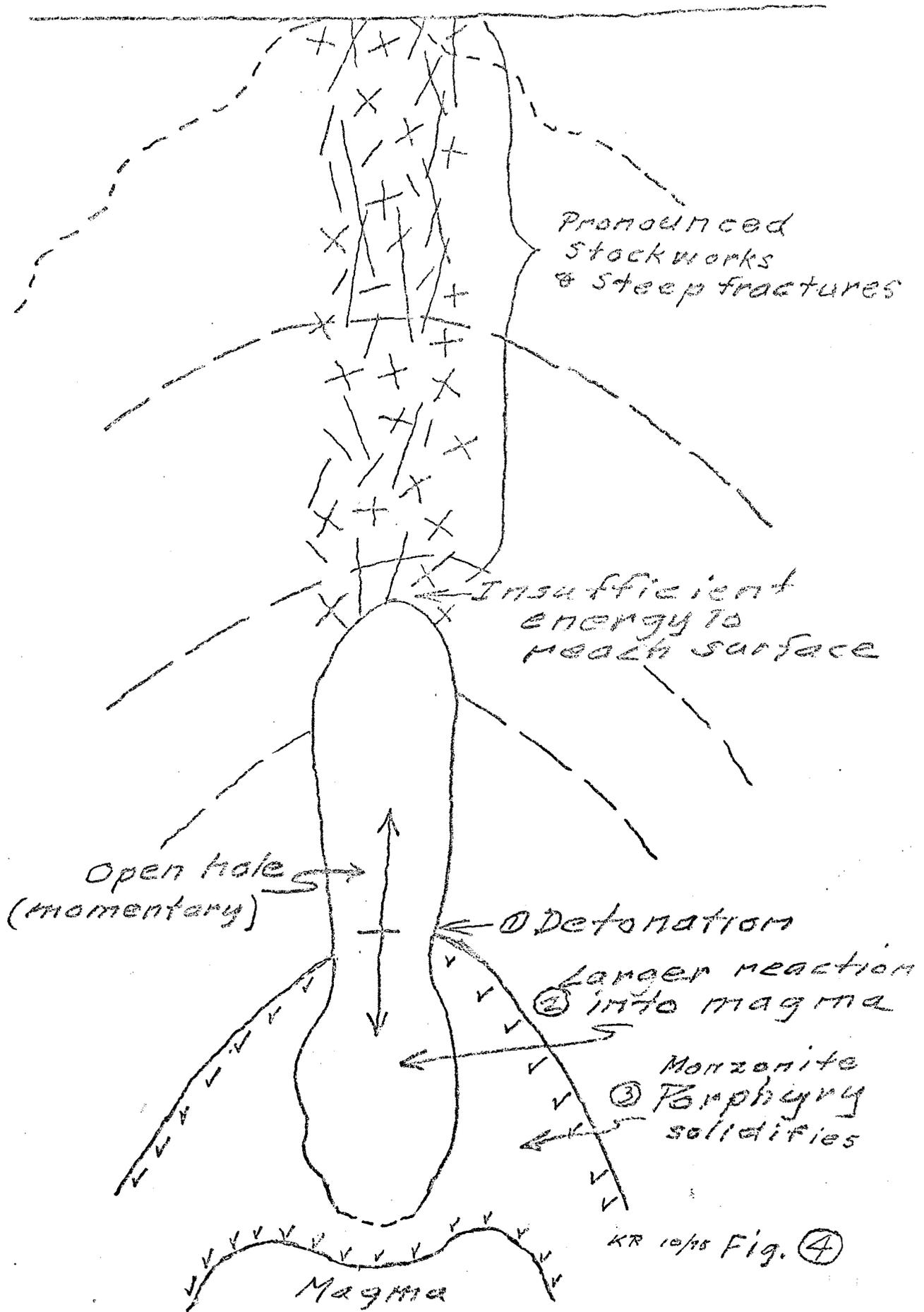
Ground surface up here somewhere



KP 10/75 Fig. (2)



KR 10/75 Fig. (3)



KR 10/15 Fig. ④

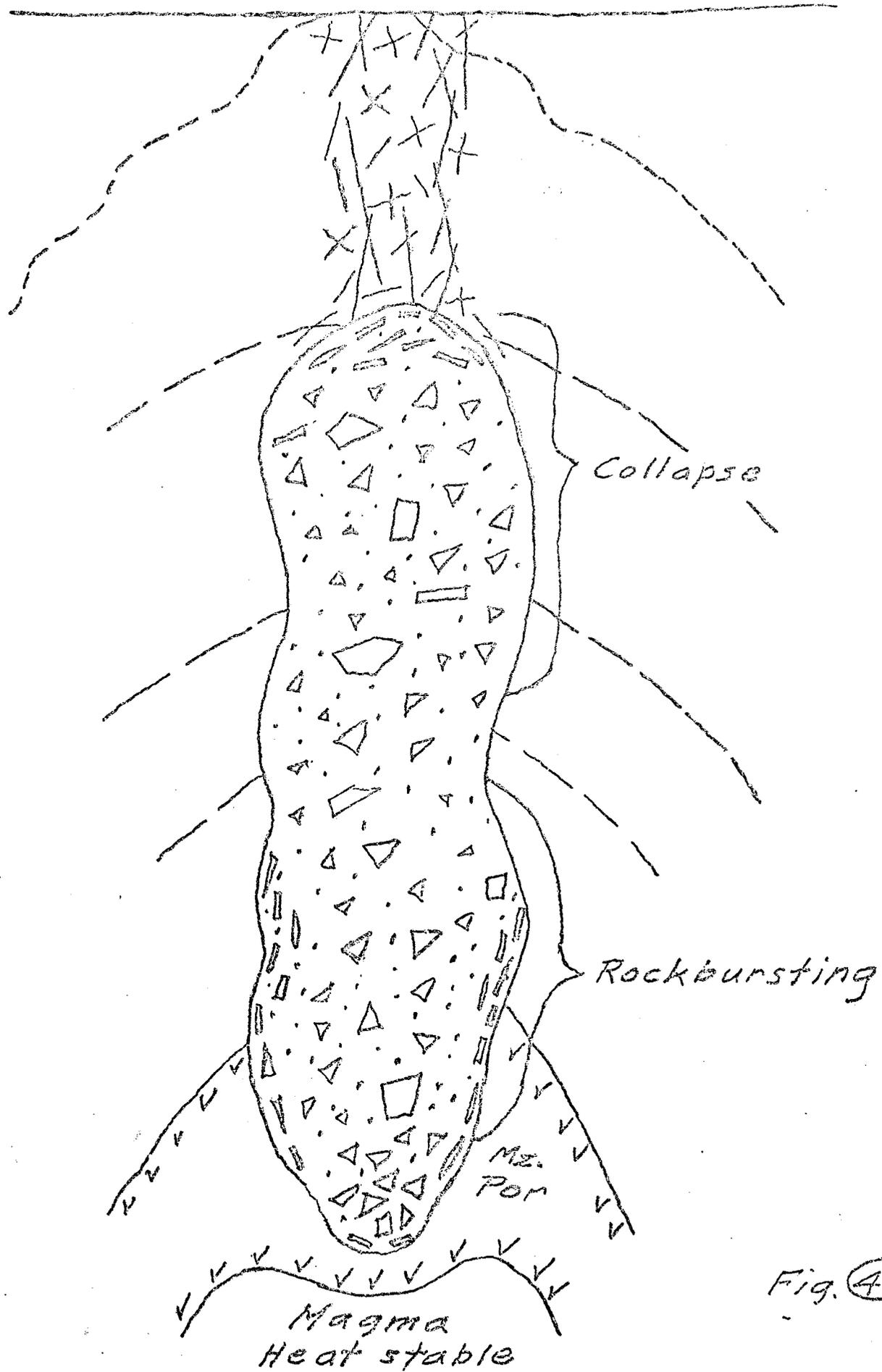
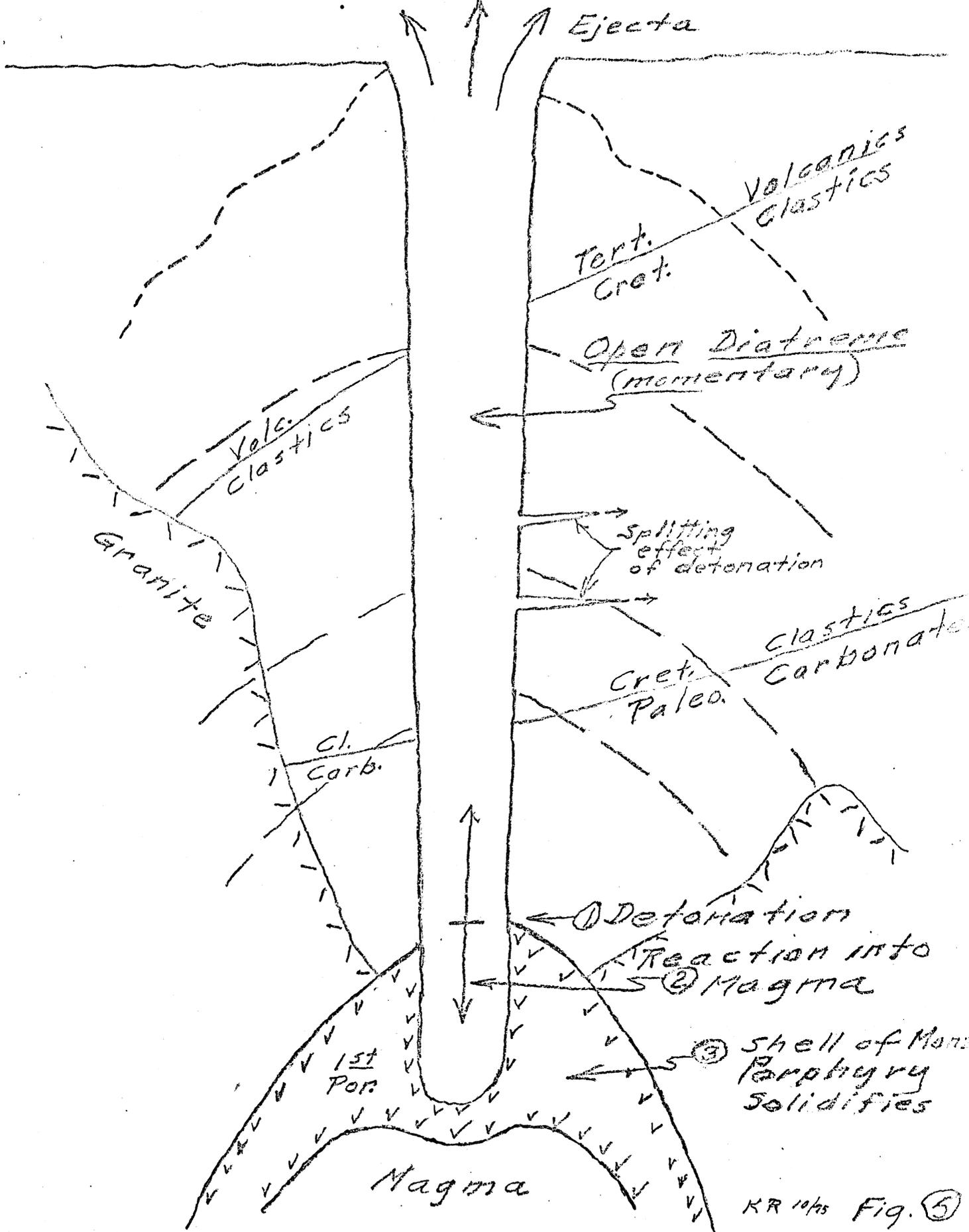
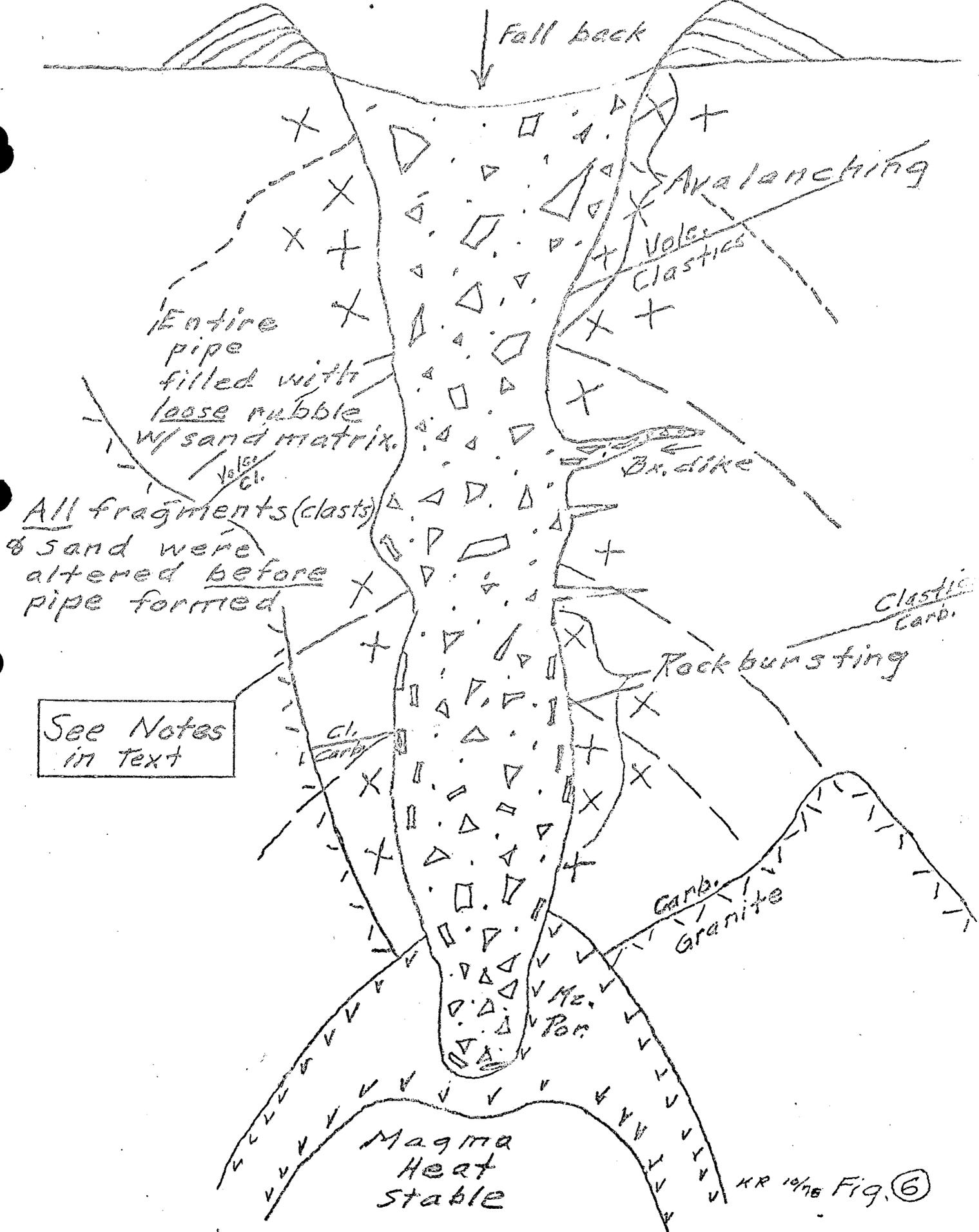


Fig. 4A

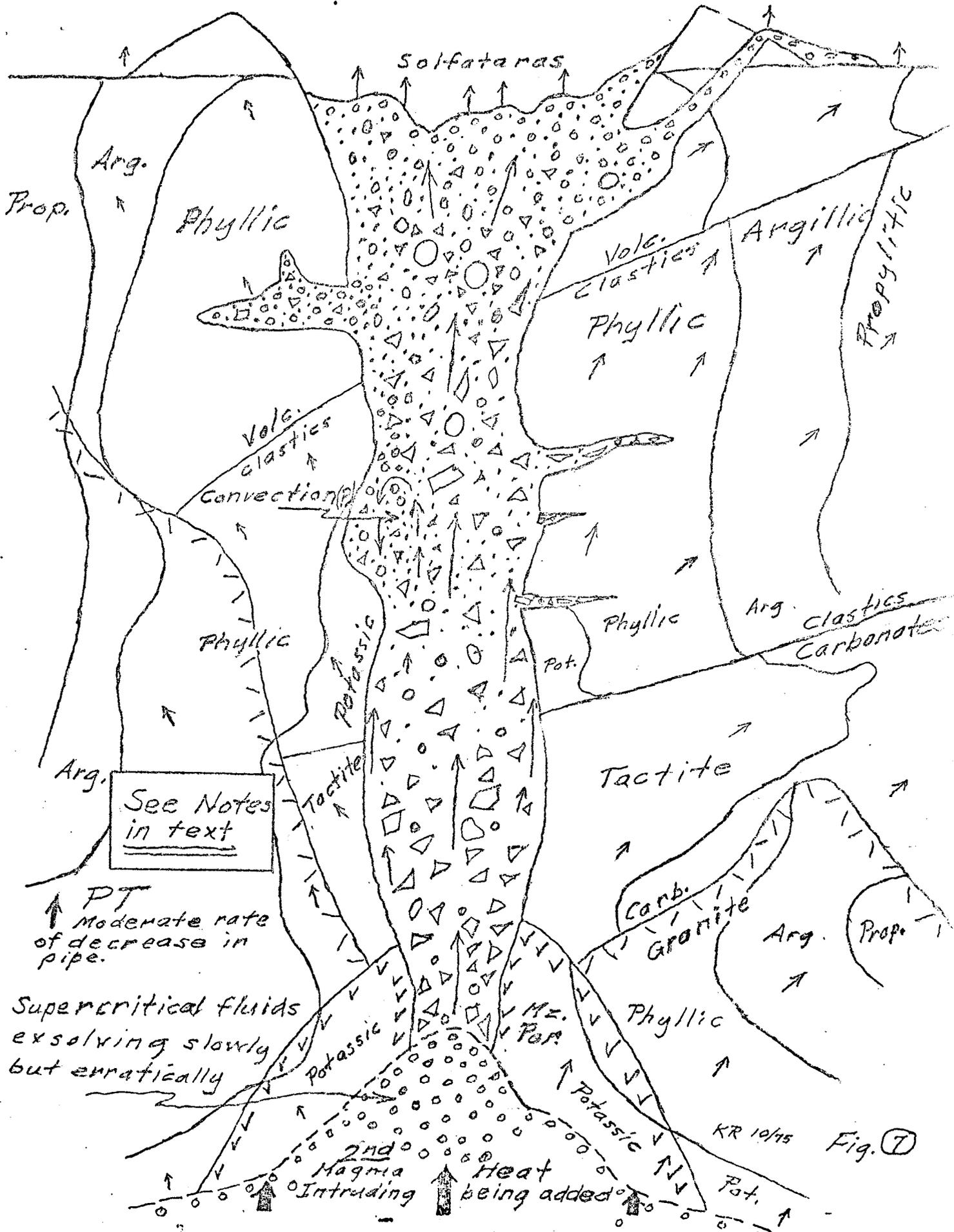


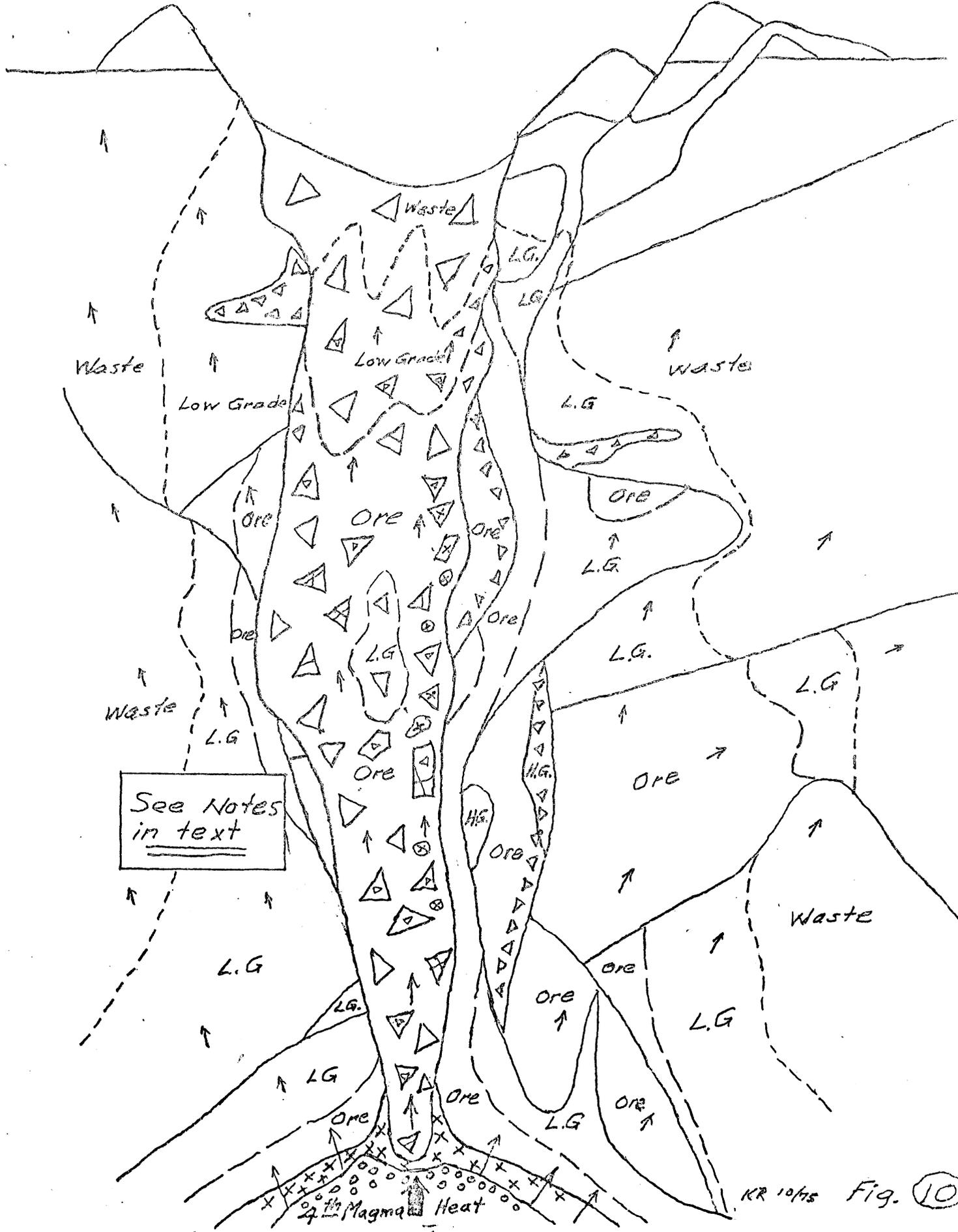
KR 1075 Fig. ⑤



See Notes
in text

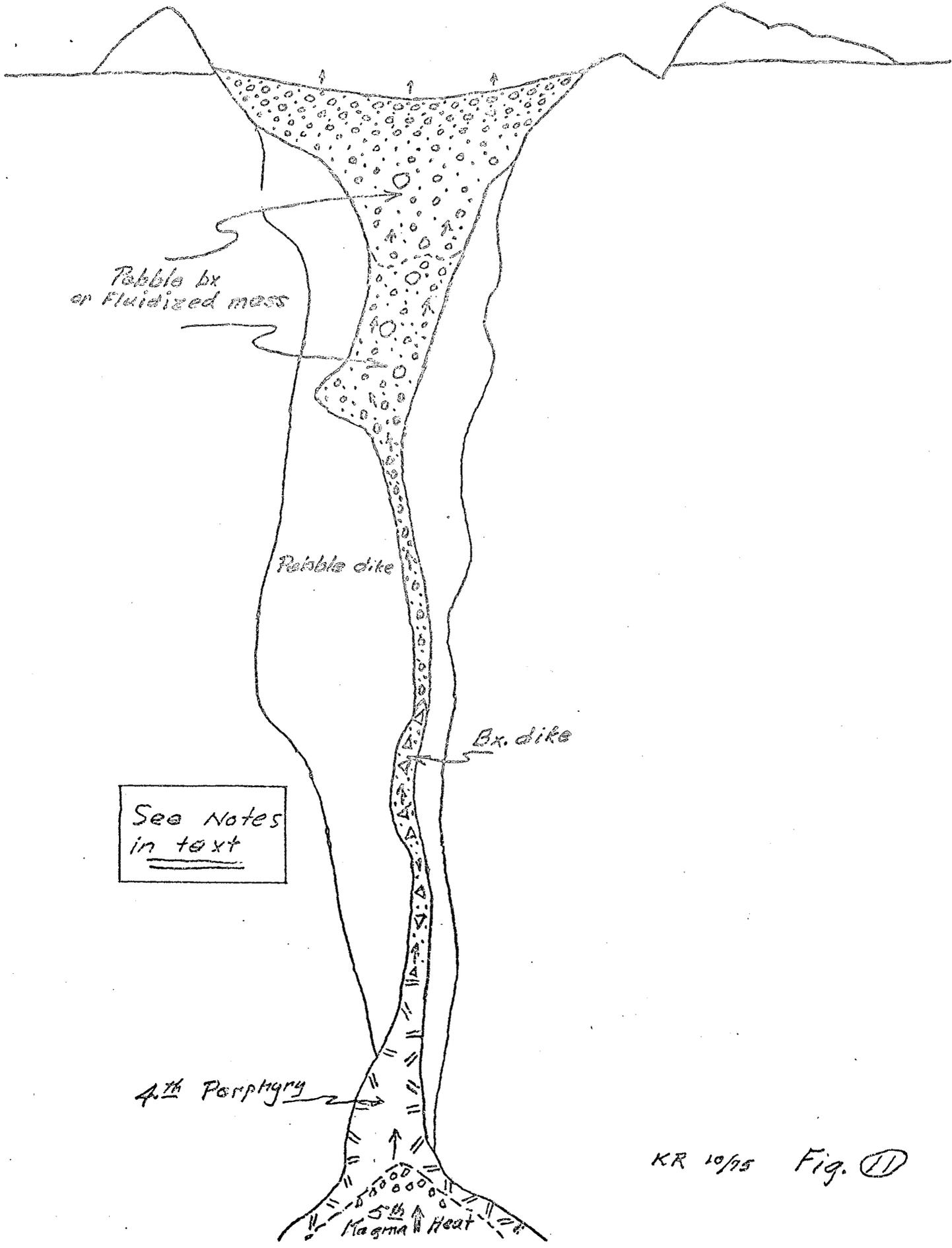
KR 10/16 Fig. 6





See Notes
in text

KR 10/75 Fig. 10



Rubble bx
or Fluidized mass

Rubble dike

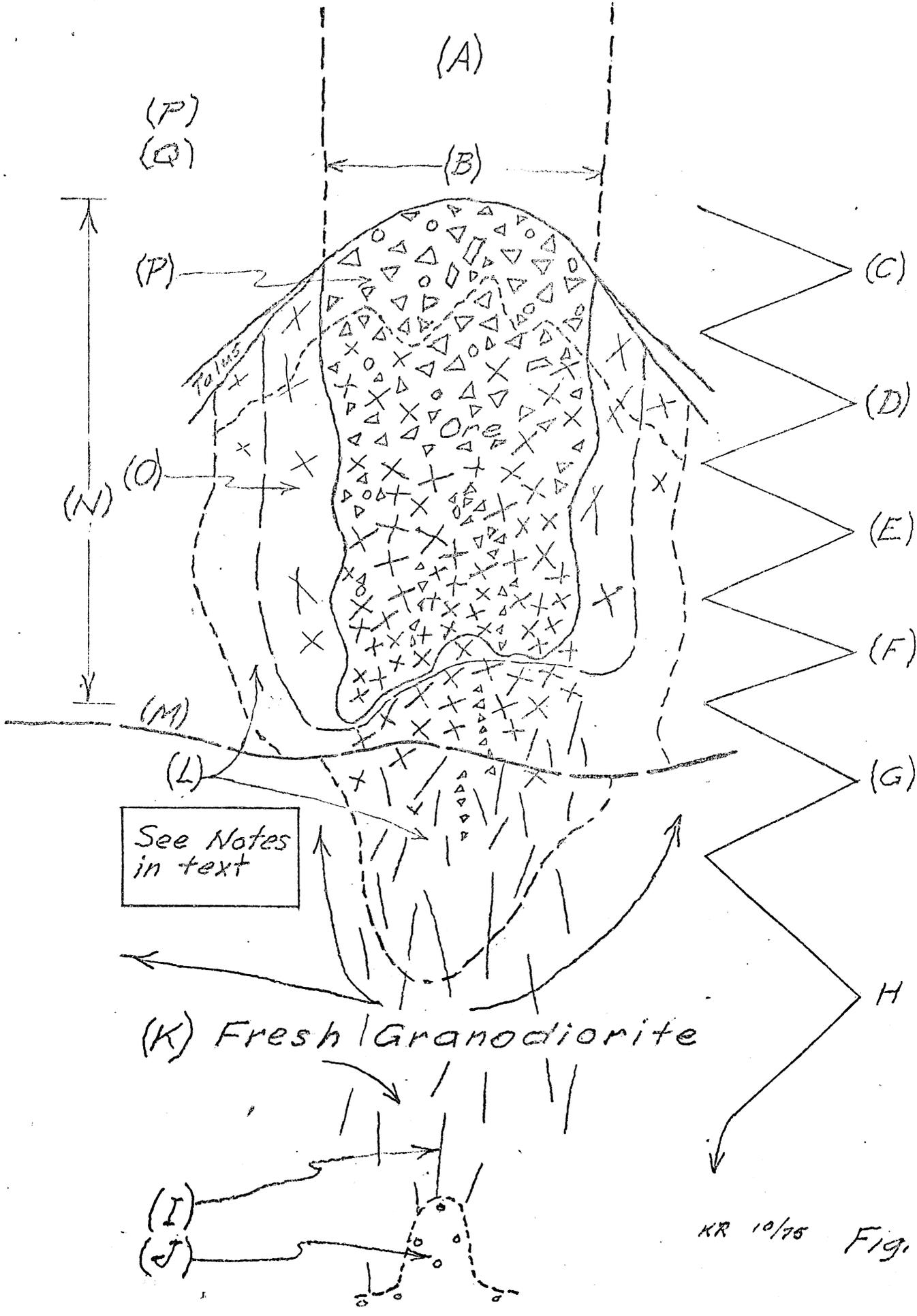
Bx. dike

See Notes
in text

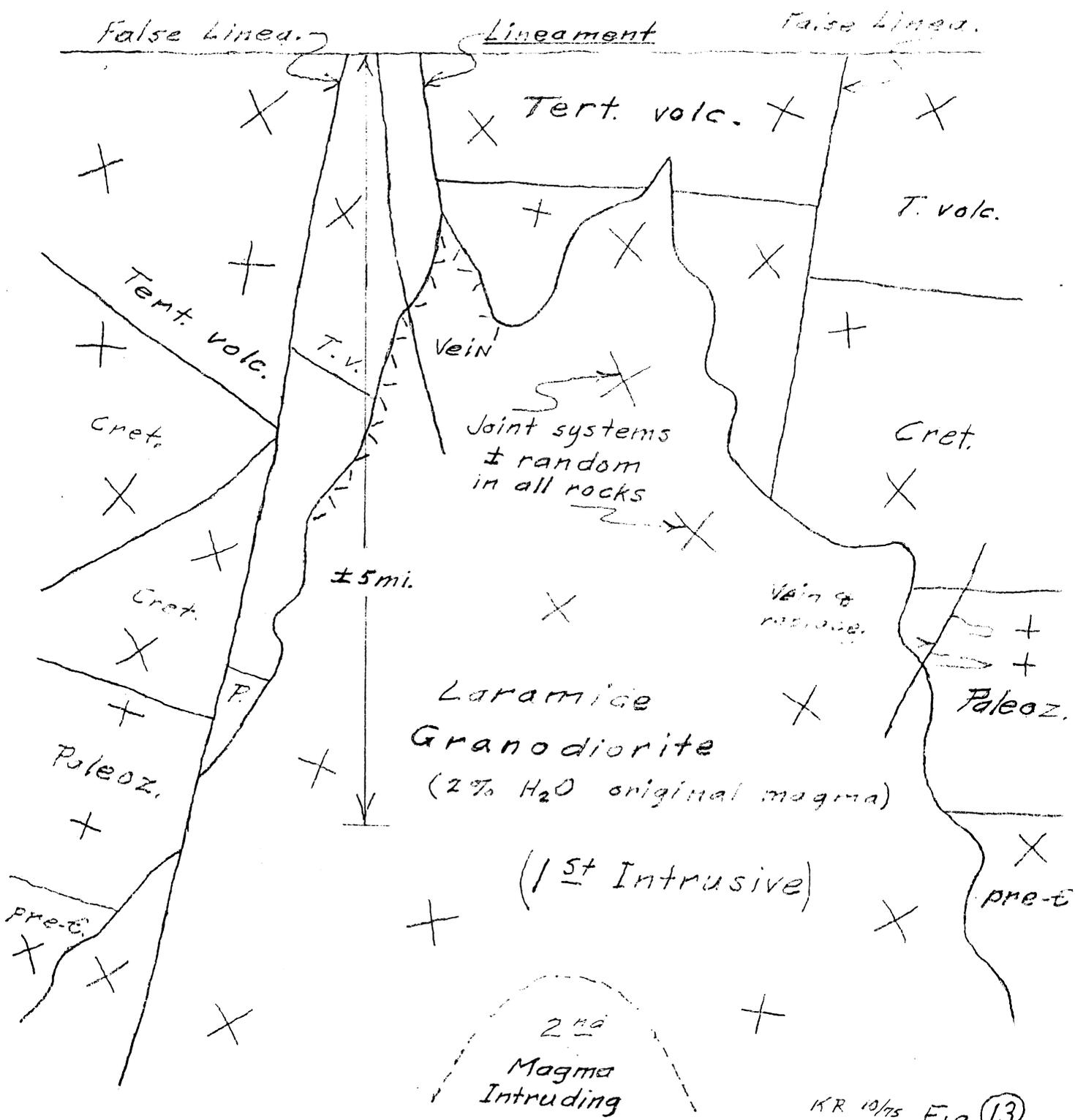
4th Porphyry

Magma Heat

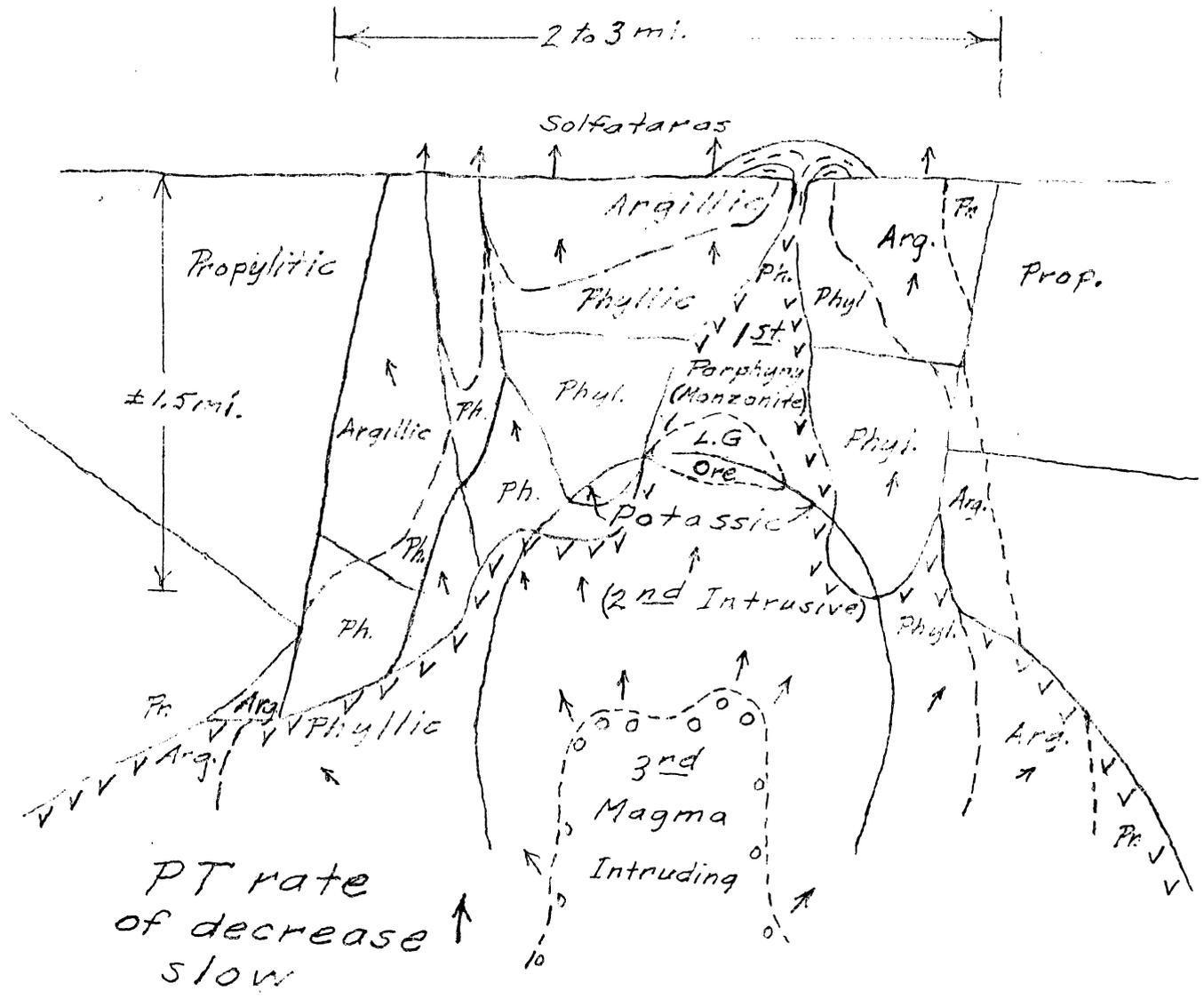
KR 10/75 Fig. ⑪



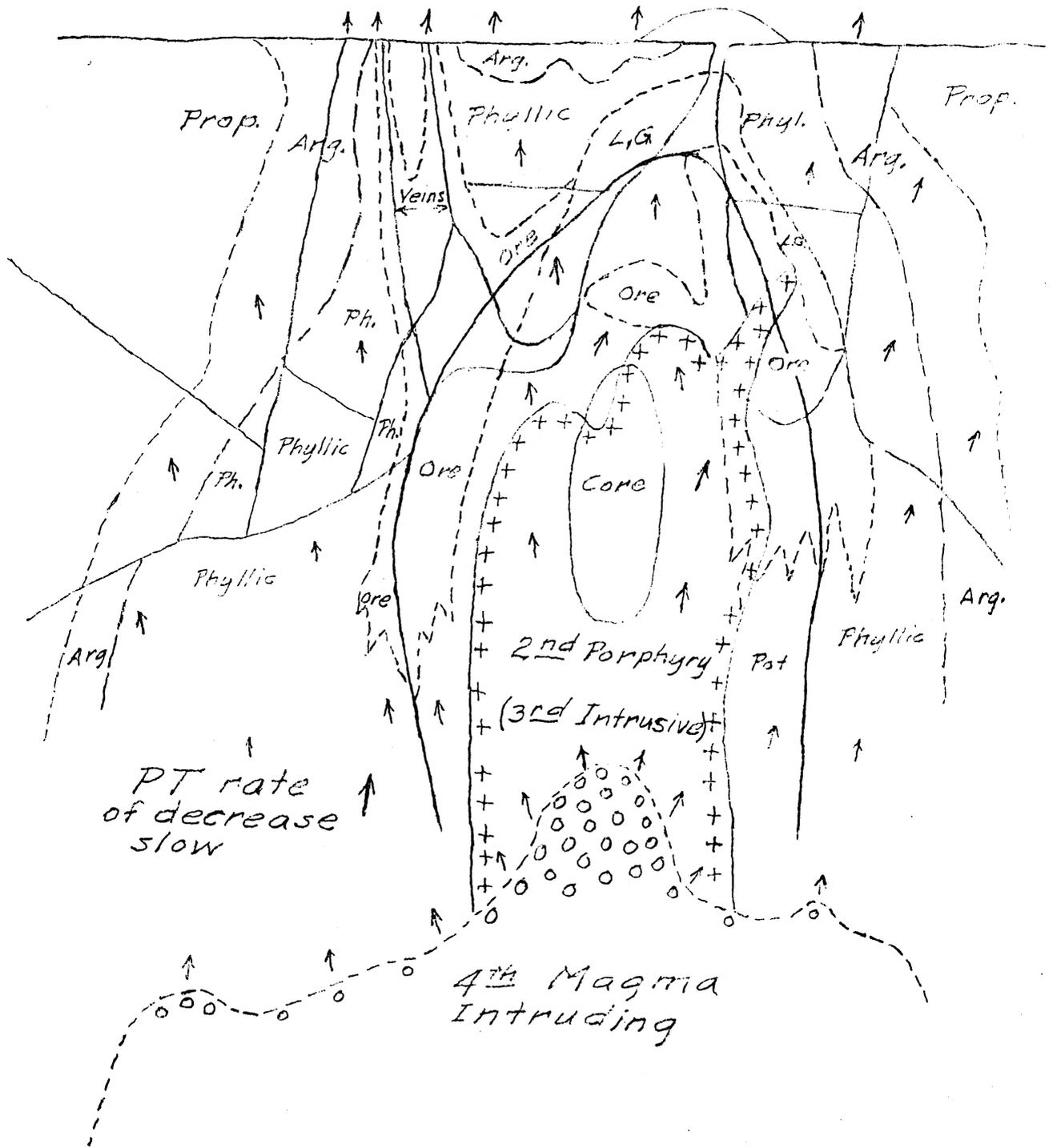
5 to 20 miles



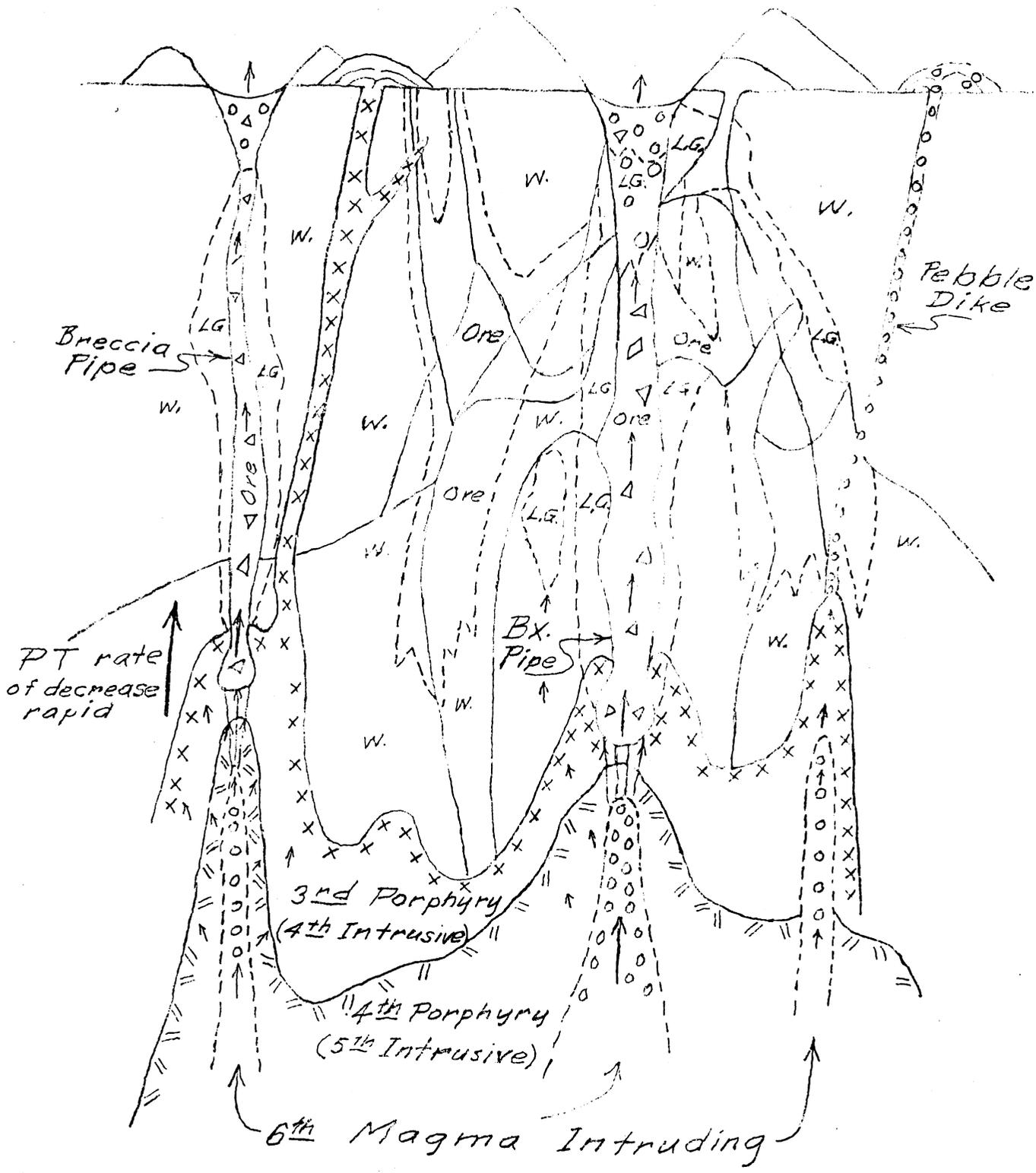
KR 10/75 Fig (13)



KR 10/75 Fig. (14)



KR 10/75 Fig. (15)



PT rate of decrease rapid

KP 10/75 Fig. 16

Geology of Toquepala, Peru

by Kenyon Richard and James H. Courtright



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METALLOGENIC ASPECTS OF PORPHYRY COPPER DISTRIBUTION

Definitions

Map Discussions

Distribution

Plate Tectonics

Brock

Russian Metallogenic Theories

Zoning

Age

Minerals

Mineral Belts

Size distribution

Mathematical and Statistical Distribution

Effect of Cover

Vegetation

Alluvium

Volcanic flows

Paul Eimon
April 15, 1975

CHANGING PATTERNS OF GLOBAL P.C.D. DISCOVERY
AND DEVELOPMENTS

History of P.C.D developments

1910 - 1925

1925 - 1950

1950 - 1960

1960 - 1970

1970 - 1975

Future

Time spans between discovery and developments

Political and Economic considerations.

Exploration factors related to techniques and geologic features

Paul I. Eimon
April 15, 1975

III

DEVELOPMENT OF NEW TARGET AREAS

Chile

Bolivia

Peru

Ecuador

Colombia

Panama

Costa Rica

Nicaragua

Honduras

Mexico

USA

Canada

Alaska

Philippines

South Pacific

Australia

India

Iran

Europe

North Africa

Paul I. Eimon
April 15, 1975

DIMENSIONS OF IDENTIFIED COPPER DEPOSITS OF THE WORLD

During the last five years, several studies appeared which contain extremely valuable information about the known copper deposits, in terms of their past production and reserves. Such information is, of course, the cornerstone of any appraisal of undiscovered resources. These studies evaluated copper deposits as follows:

<u>Investigator</u>	<u>No. of Deposits Investigated</u>	<u>Total Copper Metal Contained (Past Production + "Reserves")</u>
Pelissonnier, 1968	374	392 million short tons
Pelissonnier, 1972 (BRGM Memoir No. 57)	522, U.S.S.R. included	436 million short tons
Amax, 1970 (unpublished)	315, U.S.S.R. excluded	429 million short tons

1. Distribution by Metal Content

The Amax study indicates that the bulk of the copper in known deposits is contained in a small percentage of the deposits. Twenty-eight percent of the deposits contain 84.8% of the copper. This is summarized in Table I, where the deposits are grouped by classes. For each class, the upper tonnage limit is equal to the lower tonnage limit multiplied by the square root of 10. The information contained in Table I is graphically presented in Fig. 1, as to frequency distribution by class and, in Fig. 2, with regard to cumulative distribution. Fig. 2 shows that the first three classes of deposits (more than 1,000,000 tons metal contained) represent the major part of the copper tonnage in known deposits. In preparing resource appraisal and exploration plans, special attention must be given to an analysis of geological environments most favorable to deposits of these three classes. Deposits in Class #1, with 10-31.6 million tons of metal contained, can be described as "super-giant" deposits, whereas those in Class #2, with 3.1-10 million tons of copper contained, may be labeled as "giant" copper deposits. These two classes have provided the bulk of the past and current production.

2. Distribution by Geologic Type of Deposit

Over the years, some geologic types of copper deposits have been recognized throughout the world. No attempt is made here at defining these types, since they are pretty well accepted. For definitions, the reader is referred to U.S.G.S. Professional Paper 820, Pelissonnier's 1972 opus and Cox, 1973 paper. Table II indicates that the bulk of the known copper deposits - 89% - is contained in three geological types, with two other geologic types providing another 7 percent. This emphasizes the critical need for a detailed geologic understanding of porphyry copper and strata-bound copper deposits, the two main types (79% of copper) in preparing appraisals of undiscovered resources. On Table II, the geological age distribution of the three main types has also been shown. It appears there is a definite age range for each type. This is another geologic factor which can be used in resource appraisal of geological belts of known age.

It is interesting to note that of six deposits in Class #1, four are porphyry copper and two are strata-bound; in 40 deposits in Class #2, 28 are porphyry copper, nine strata-bound, two massive sulfides and one associated with basic-ultrabasic rocks. Thus, the two main geologic types of deposits provide the largest deposits.

The U.S.G.S. has made a study of size and grade characteristics of selected copper deposits by geologic type and location. Results published in Professional Paper 820 are shown in Fig. 3; they confirm that porphyry copper and strata-bound provide the largest deposits with, however, some marked differences in size, in different parts of the world.

3. Porphyry Copper Deposits

This type of deposit represents over 50% of the metal tonnage in known deposits. The U.S.G.S. has started a detailed analysis of this type. Porphyry coppers discovered in the U.S. and Canada, after 1960, are generally of lower grade than those known in the U.S.A., previous to 1960. Such historical trend is important in making a resource appraisal of recently identified new districts and provinces where only one, or a few discoveries have been made.

Recent discoveries in (1) a poorly explored copper belt, such as La Caridad in Sonora, Mexico, and (b) a new copper belt such as Bougainville Island, indicate that in such cases the metal content and the ore tonnage and grade can be as high as in the giant deposits of well-explored porphyry copper districts. After assembling the data for Professional Paper 820, the U.S.G.S. continued its inventory of known copper deposits. Recent results are shown in Fig. 4. This graph reveals that the copper tonnage in known deposits is actually much larger than reported in Professional Paper 820. No correlation is apparent between tonnage and grade within any of the three populations of porphyry, strata-bound and massive sulfide copper deposits.

The porphyry population was the object of a special analysis by the U.S.G.S. It would appear that both tonnage and grade have a geologic upper limit and an economic lower limit changing with time. The wide scatter of tonnage at each grade level can be expected for lower grade levels. This means, however, that total metal content of lower grade deposits will also be lower than for deposits known to date.

Other results of this U.S.G.S. study are shown in Fig. 5 and Table III. This study confirms that recent discoveries are, on the average, much lower in grade than discoveries made prior to 1960. For instance, the median dimensions of a group of 19 pre-1960 porphyry coppers are 495 million tons of 0.84% copper ore containing 4.2 million tons copper metal. This can be compared to median values for a group of 78 selected porphyry coppers known to date of 246 million tons of 0.73% copper ore with a metal content of 1.8 million tons. This illustrates that, in most areas, the first discoveries are the largest. This is explained by the fact that, in comparison with the smaller deposits found later, the larger dimensions of the first discovery allow greater chances of surface expression of mineralization and, therefore, easier discovery. Table III illustrates again what Fig. 3 pointed to: there are variations in grade and tonnage of porphyry coppers depending on location.

The bimodal grade distribution (Fig. 5) is explained by the process of secondary surficial enrichment superimposed on primary copper deposition processes. The tonnage displays a unimodal distribution.

With a view to exploration planning, Amax analyzed the size distribution of porphyry copper deposits in two parts of the North American Cordilleras. Fig. 6 shows that British Columbia and the Yukon, to date, do not contain any giant, or super-giant deposits, whereas Arizona and southwestern New Mexico contain quite a few giant deposits.

TABLE I

WORLD COPPER DEPOSITS (past production + ore reserves), EXCLUDING U.S.S.R.
(as of 1970)

Tonnage Limits (1000 tons metal)	Class of Deposit	Number of Deposits in each class	Total Copper contained in each class (1000 tons metal)	Average Copper Content per Deposit (1000 tons metal)	Cumulative Percentage of Total Number of Deposits %	Cumulative Percentage of Total Copper Contained %
31,623						
10,000	#1	6	103,849	17,308	1.9	24.2
3,162	#2	40	173,474	4,448	14.3	64.7
1,000	#3	45	86,313	1,876	28.9	84.8
316	#4	81	48,157	595	54.6	96.0
100	#5	68	13,623	200	76.2	99.2
32	#6	52	3,021	58	92.7	99.8
10	#7	22	519	24	99.7	99.9
3	#8	1	9	-	100.0	100.0
	<u>Total</u>	315	428,965			

TABLE I

MAIN GEOLOGIC TYPES OF COPPER DEPOSITS (After Pelissonnier, 1963, 1972)
AND THEIR GEOLOGIC AGES (after Ch. Meyer, unpublished)

	<u>% Tonnage Metal Contained</u>		<u>Geologic Age Range</u>
	<u>1968</u>	<u>1972</u>	
PORPHYRY COPPERS	51.8	52.4	Mostly 130 to 1 Mn.yrs. Some in Paleozoic: 300-500 Mn. yrs.
STRATA-BOUND COPPERS (In Sedimentary Rocks)	26.5	26.9	Mostly 1800-500 Mn.yrs. (A few 500-200 Mn. yrs.; one recent)
MASSIVE SULFIDES (in Volcanic Assemblages)	10.7	9.9	Mostly 3200-1800 Mn.yrs.. (none between 1800 and 500 Mn.yrs. A few very recent.)
	89.0%	89.2%	
IN BASIC AND ULTRABASIC ROCKS	2.9	4.7	
IN INTERMEDIATE BASIC LAVAS	<u>2.7</u>	<u>2.3</u>	
	5.6%	7.0%	
OTHER TYPES	<u>5.4</u>	<u>3.8</u>	
	100.0%	100.0%	

TABLE III

MEDIAN TONNAGE, GRADE AND COPPER CONTENT OF PORPHYRY COPPER DEPOSITS

(including past production + "reserves") (After U.S.G.S.)

	<u>Number of Deposits</u>	<u>Size in million short tons ore</u>	<u>Grade % Cu</u>	<u>Copper Content in million short tons copper contained</u>
<u>All Porphyry Copper Deposits</u>	<u>78</u>	<u>246</u>	<u>.73</u>	<u>1.8</u>
U.S. and Mexico	39	268	.72	1.9
Canada	15	206	.53	1.1
Andes and Pacific	24	238	.93	2.2
<u>Pre-1960 Porphyry Copper Deposits</u>	19	495	.84	4.2

TABLE IV

MAIN COPPER PROVINCES OF THE WORLD

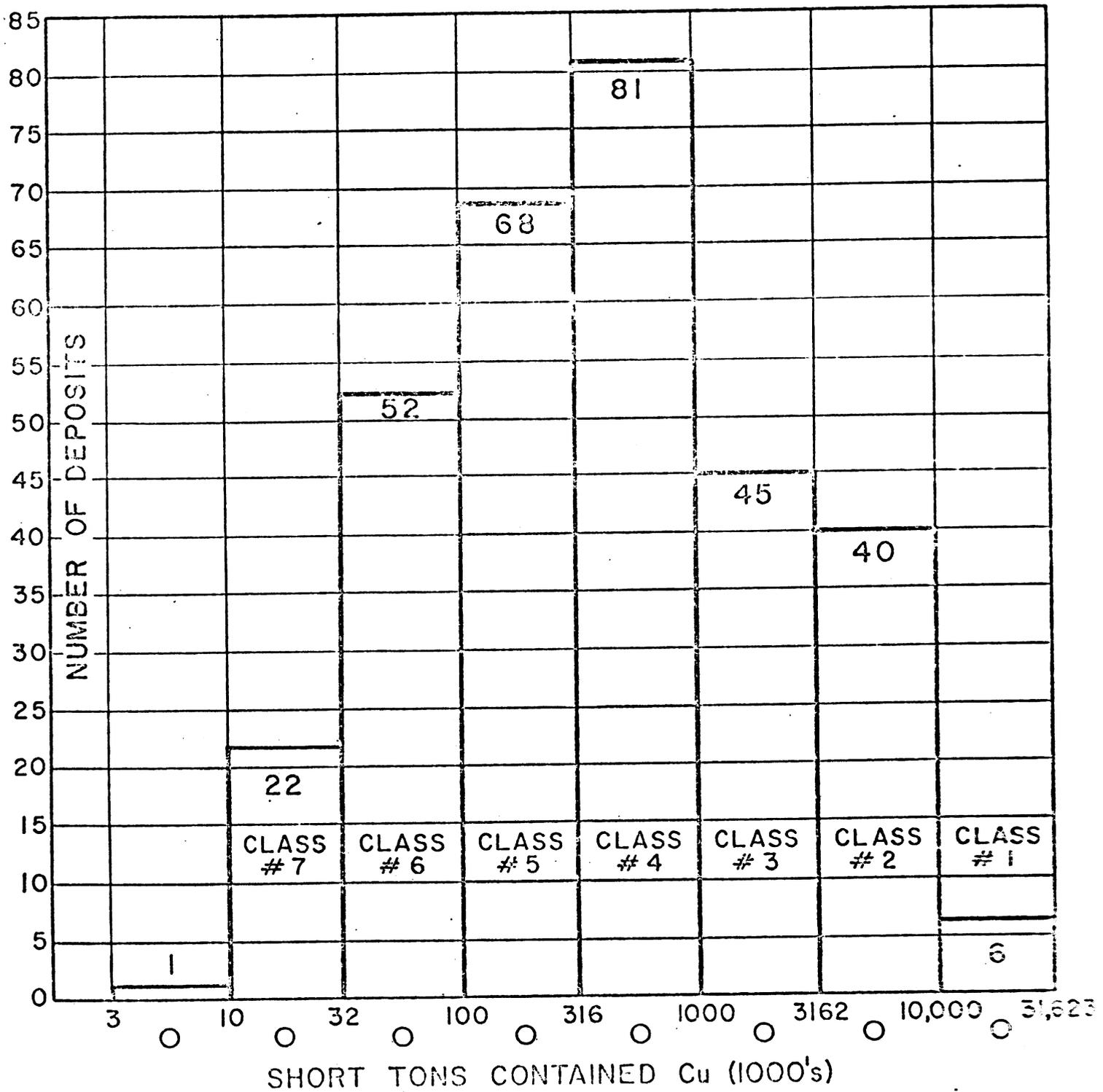
Percent Distribution of Copper Metal (after Pelissonnier, 1972)

<u>COPPER PROVINCES (PELISSONNIER, 1972)</u>	<u>% OF COPPER IN ALL PROVINCES</u>	<u>MAIN TYPES OF DEPOSITS</u>
I ANDEAN	28.8	PORPHYRY COPPERS
II N. AMERICAN CORDILLERAN	22.7	PORPHYRY COPPERS
III SOUTH CENTRAL AFRICA	19.3	STRATA-BOUND
IV N. AMERICAN GREAT LAKES	8.2	MASSIVE SULFIDES, STRATA-BOUND AND BASIC ROCKS
V NORTHERN EUROPE	8.5	STRATA-BOUND AND MASSIVE SULFIDES
VI URAL-KAZAKSTAN	4.1	PORPHYRY COPPERS, MASSIVE SULFIDES AND STRATA-BOUND
VII EAST MEDITERRANEAN	2.2	MASSIVE SULFIDES AND PORPHYRY COPPERS
VIII HUELVA, SPAIN	1.8	MASSIVE SULFIDES
IX PHILIPPINES	1.3	PORPHYRY COPPERS
X JAPAN	1.9	MASSIVE SULFIDES
XI EASTERN AUSTRALIA	<u>1.2</u>	STRATA-BOUND AND MASSIVE SULFIDES
	100.0%	

THIS REPRESENTS 98% OF
COPPER INVENTORIED IN
THE WORLD BY PELISSONNIER.

FREQUENCY DISTRIBUTION, WORLD Cu DEPOSITS (EXCLUDING USSR)

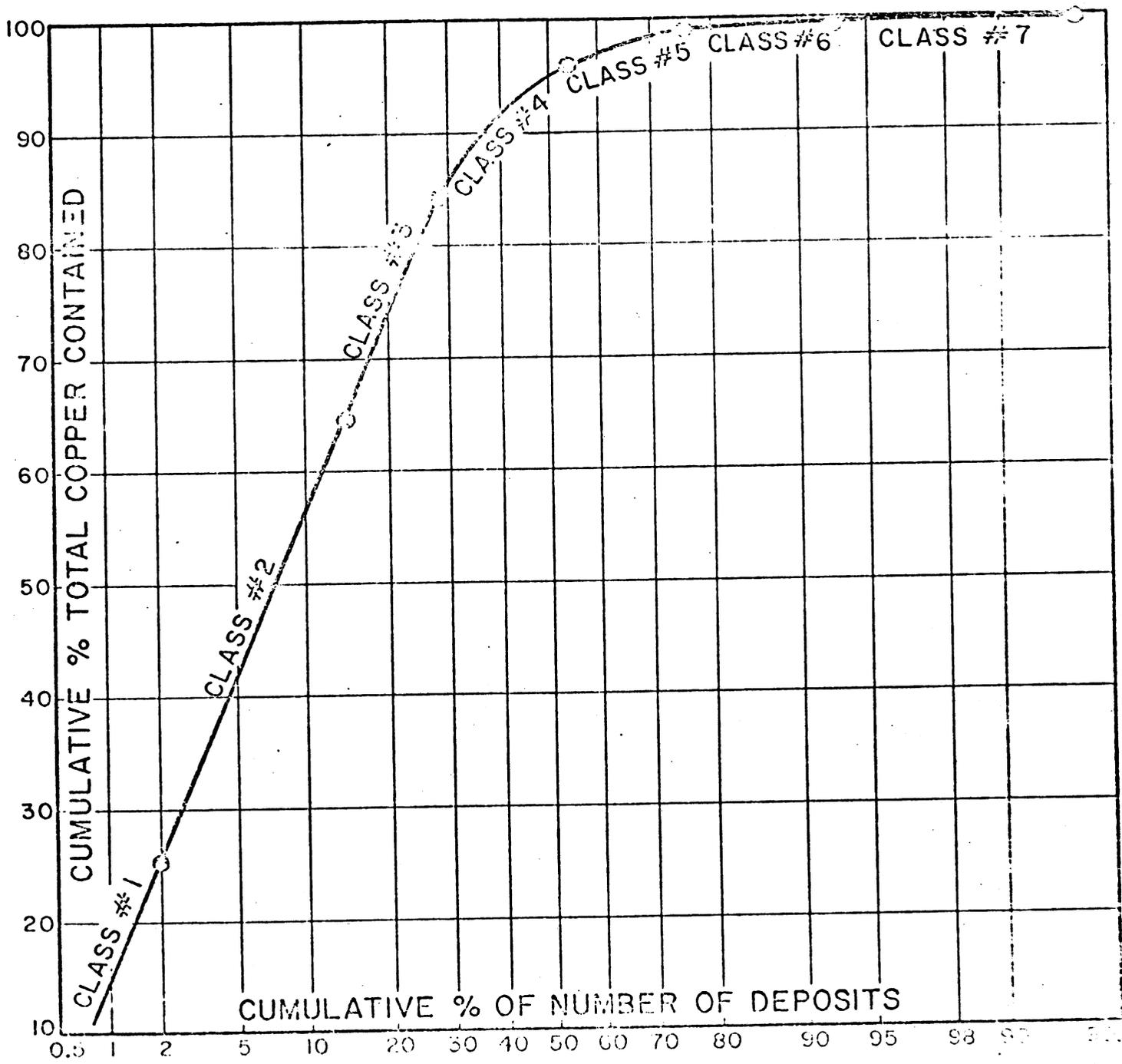
315 DEPOSITS AS OF 1970



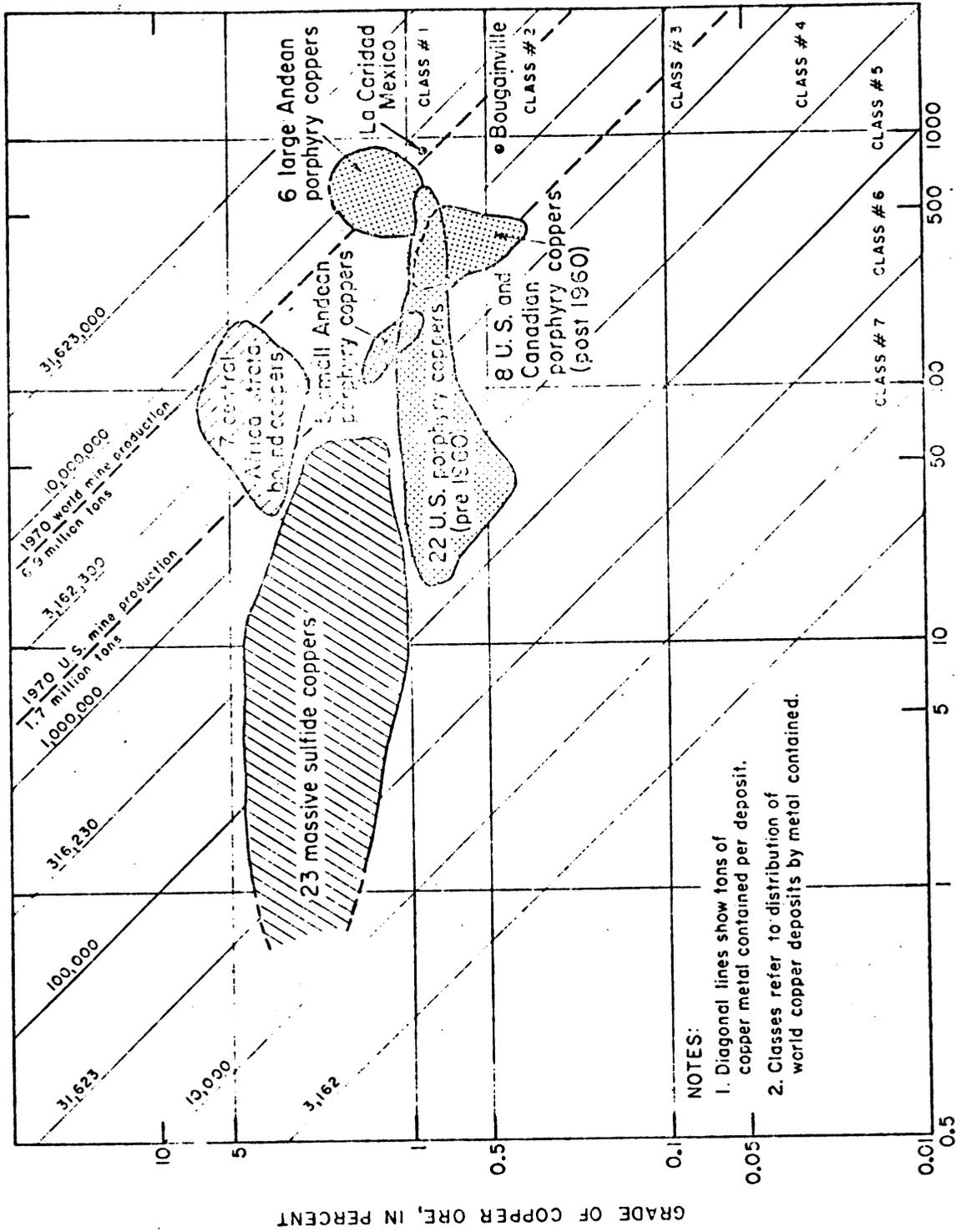
(data from AMAX unpublished study)

○ : usable for color coding correlation with maps showing location of deposits

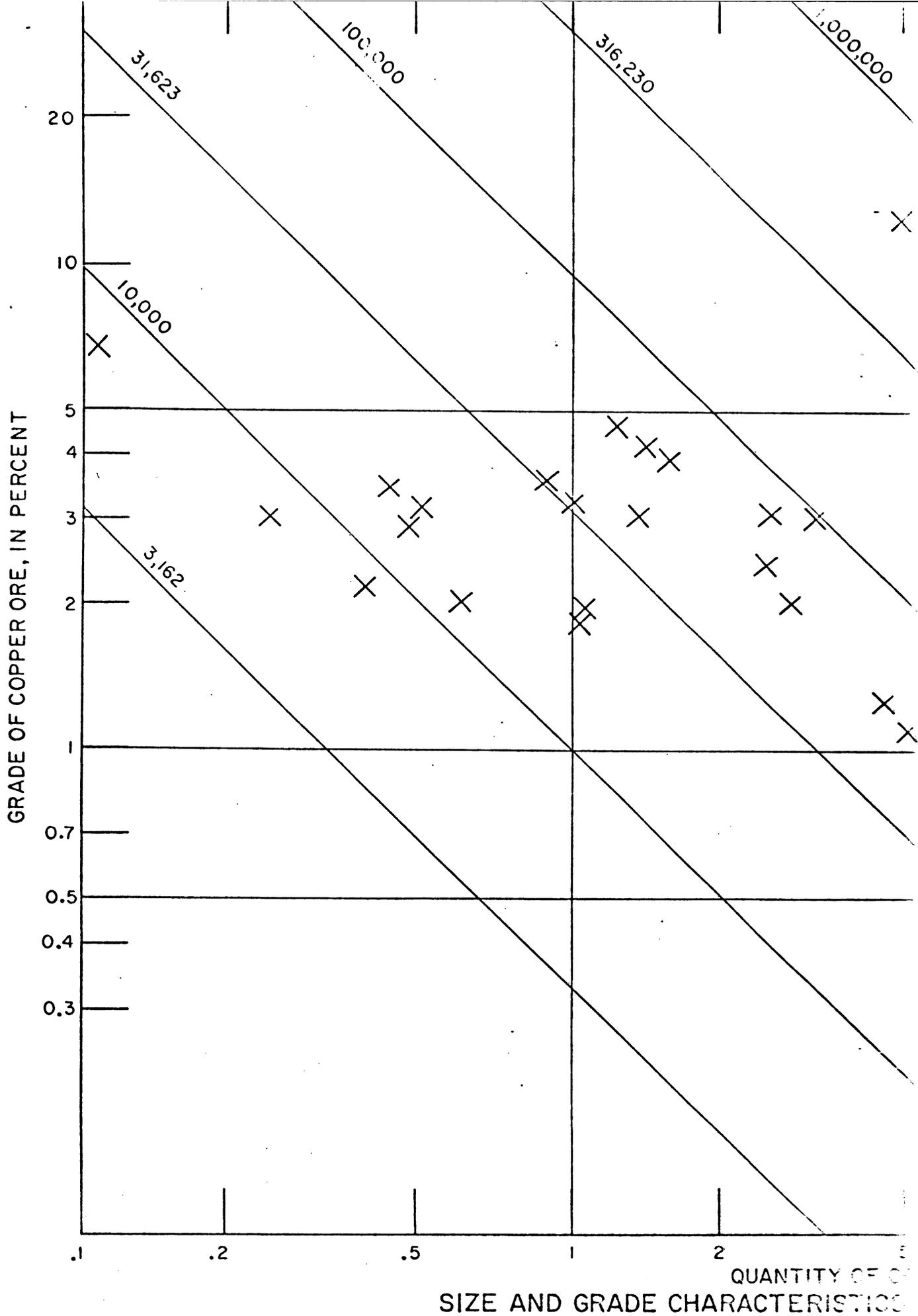
CUMULATIVE FREQUENCY DISTRIBUTION OF WORLD COPPER DEPOSITS (EXCLUDING USSR) 315 DEPOSITS AS OF 1970



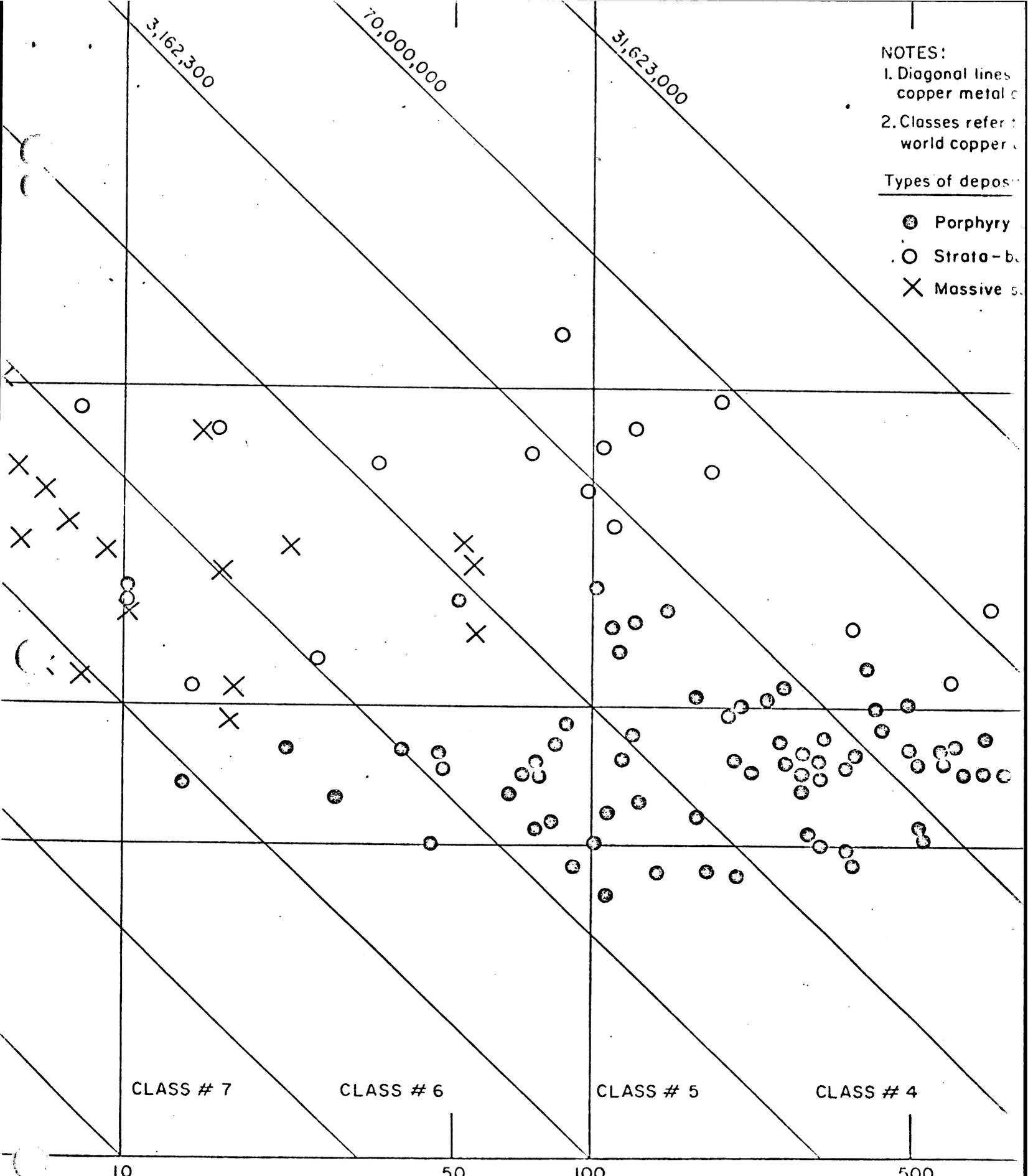
(data from AMAX unpublished study)



SIZE AND GRADE CHARACTERISTICS OF MAIN TYPES OF COPPER DEPOSITS (after USGS)



SIZE AND GRADE CHARACTERISTICS



COPPER ORE, IN MILLIONS OF SHORT TONS (past production and reserves)
 OF COPPER DEPOSITS OF THE THREE MAIN GEOLOGICAL TYPES (after USGS)

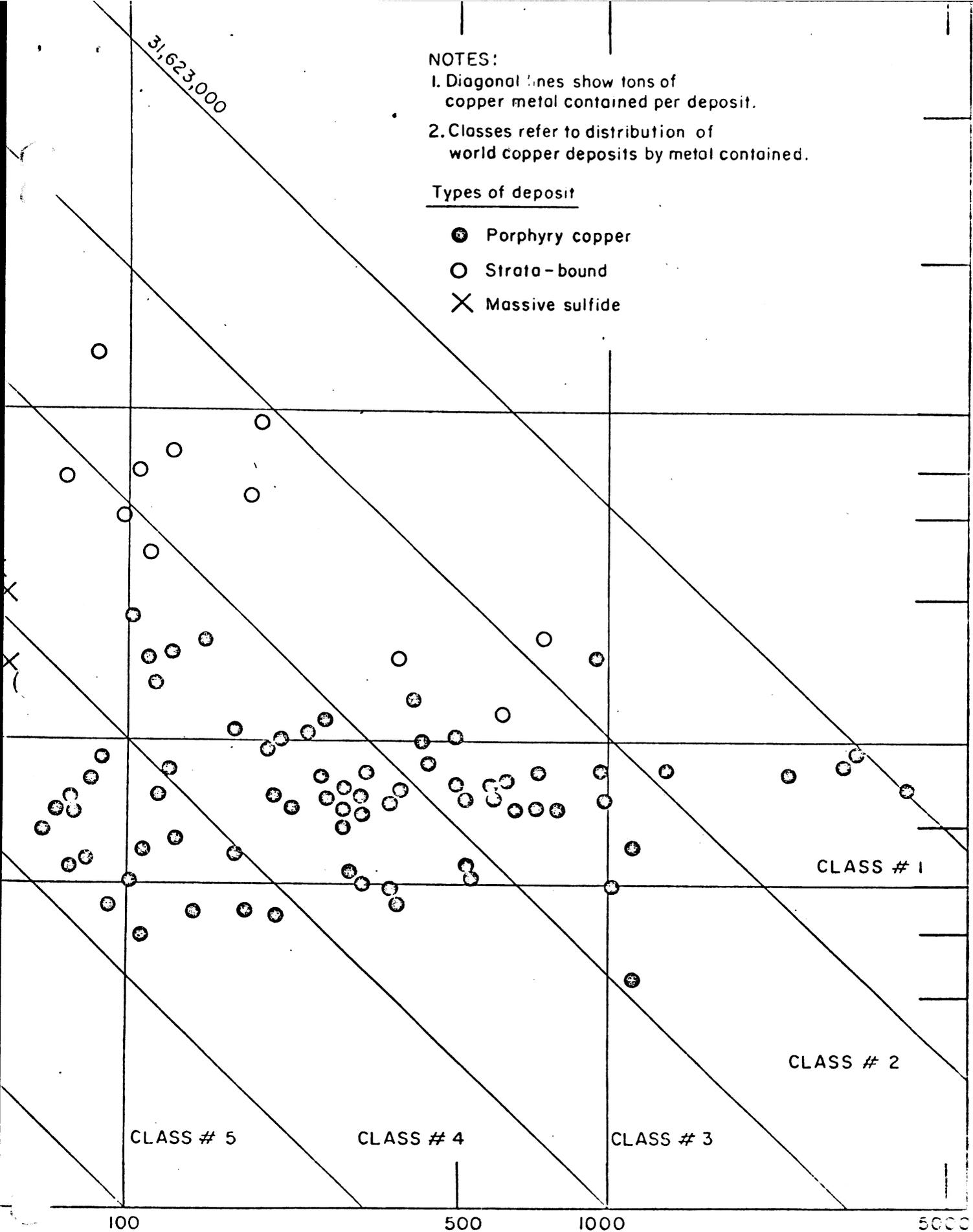
31,623,000

NOTES:

- 1. Diagonal lines show tons of copper metal contained per deposit.
- 2. Classes refer to distribution of world copper deposits by metal contained.

Types of deposit

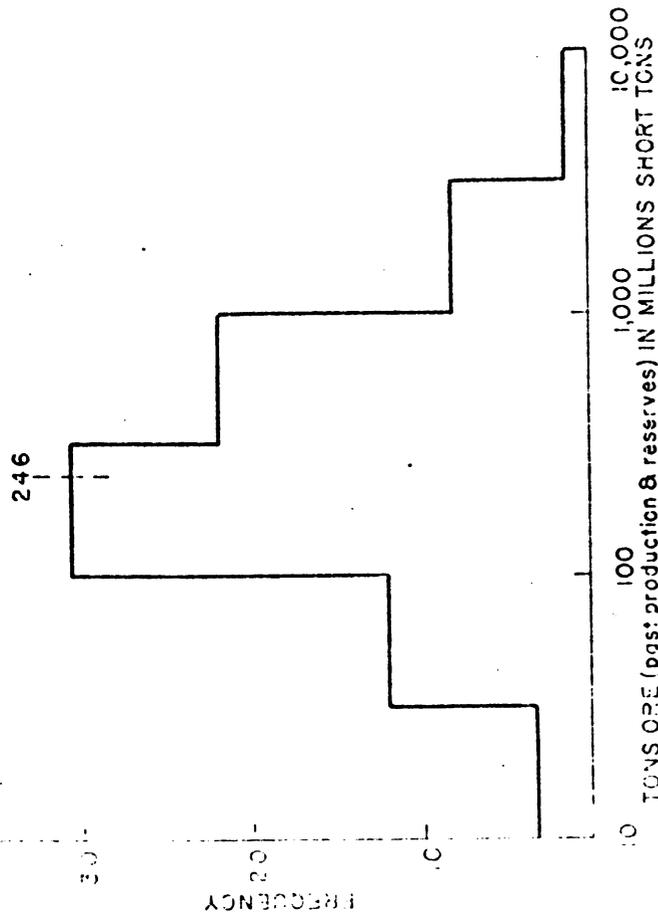
- ⊙ Porphyry copper
- Strata-bound
- × Massive sulfide



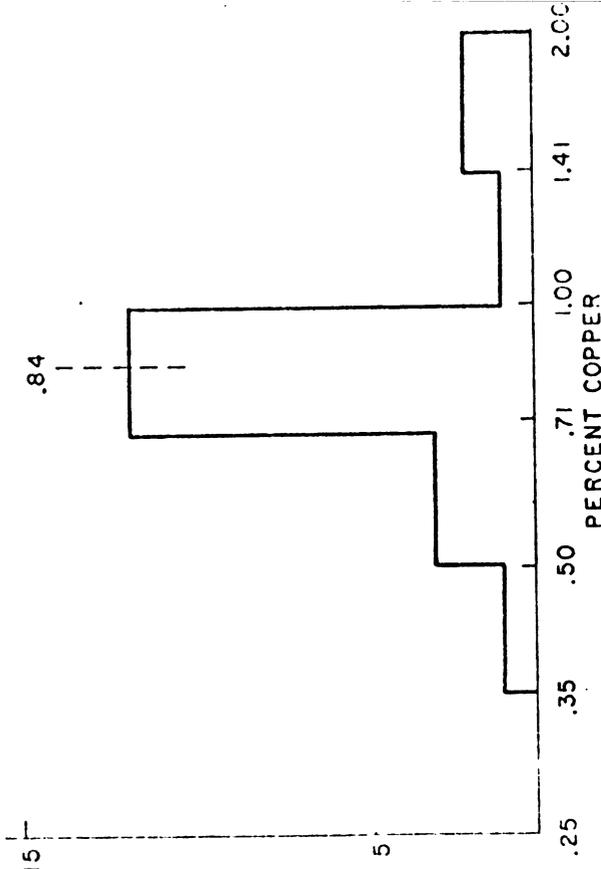
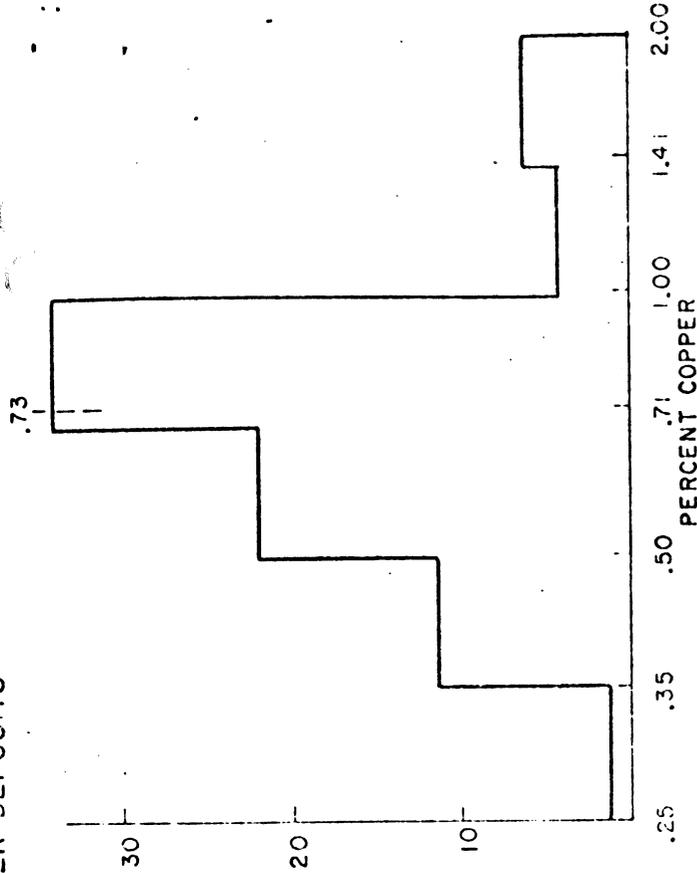
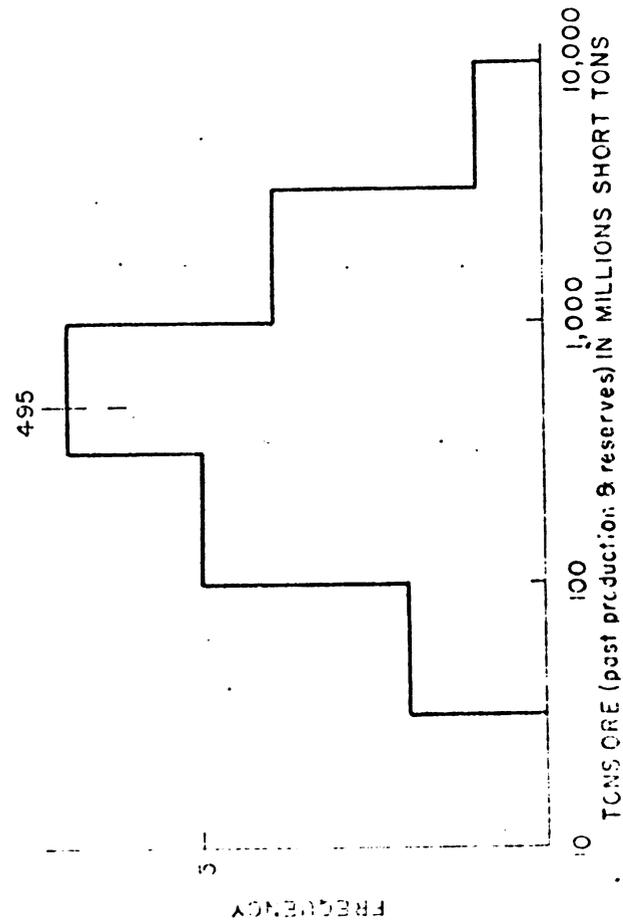
(production and reserves)

MAIN GEOLOGICAL TYPES (after USGS)

PORPHYRY COPPER DEPOSITS

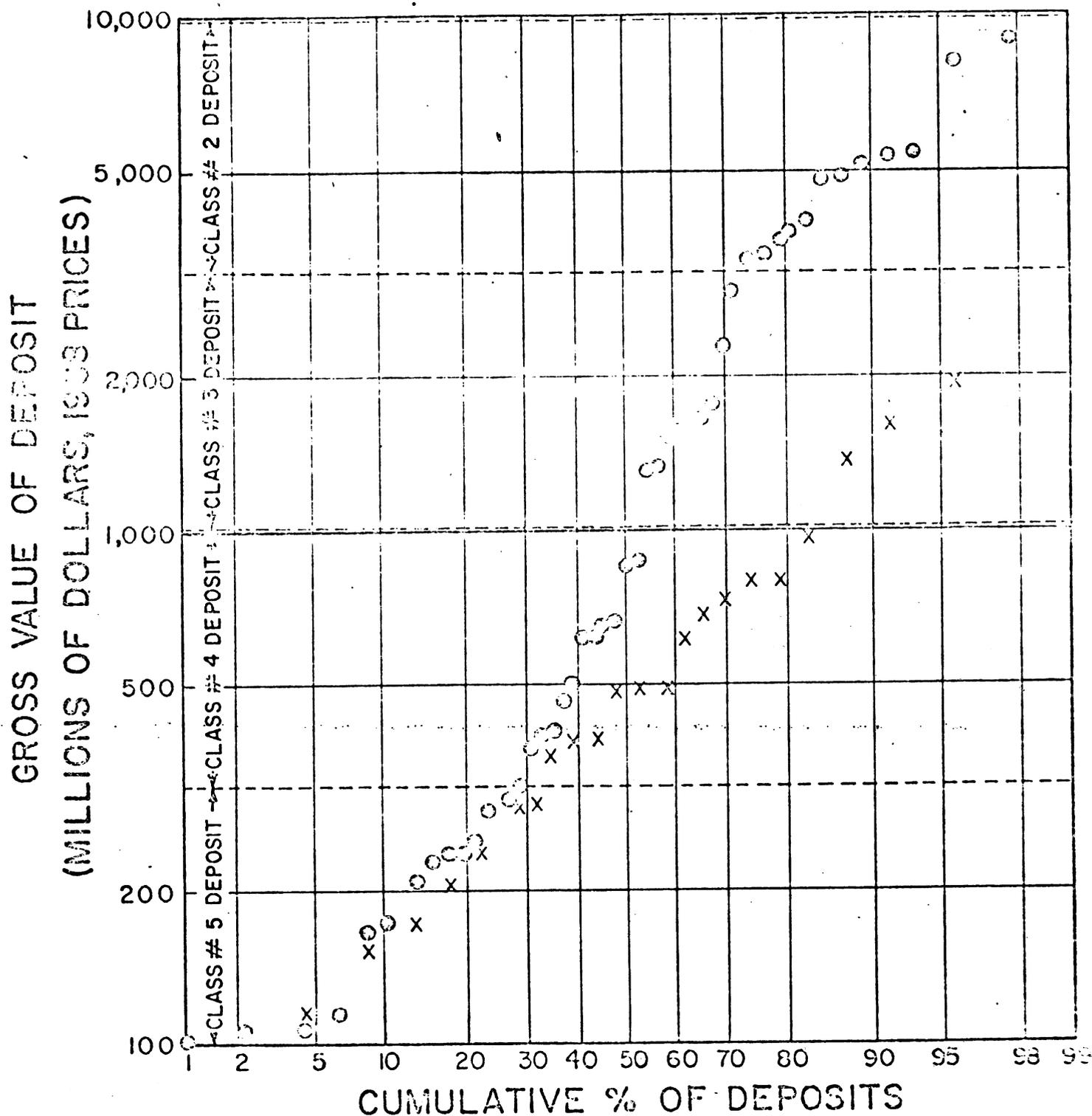


PRE-1960 PORPHYRY COPPER DEPOSITS



FREQUENCY DISTRIBUTION OF TONNAGE AND GRADE OF PORPHYRY COPPER DEPOSITS (after USGS). MEDIAN VALUES ARE INDICATED.

IN 2 PARTS OF THE NORTH AMERICAN CORDILLERAS COPPER PROVINCE



○ ARIZONA AND SOUTHWESTERN NEW MEXICO
 X BRITISH COLUMBIA AND YUKON
 (data from AMAX unpublished study)

PORPHYRY COPPER DEPOSITS IN NORTH AMERICA

○ PRODUCING MINE RECOGNIZED AS P. C. BEFORE 1950

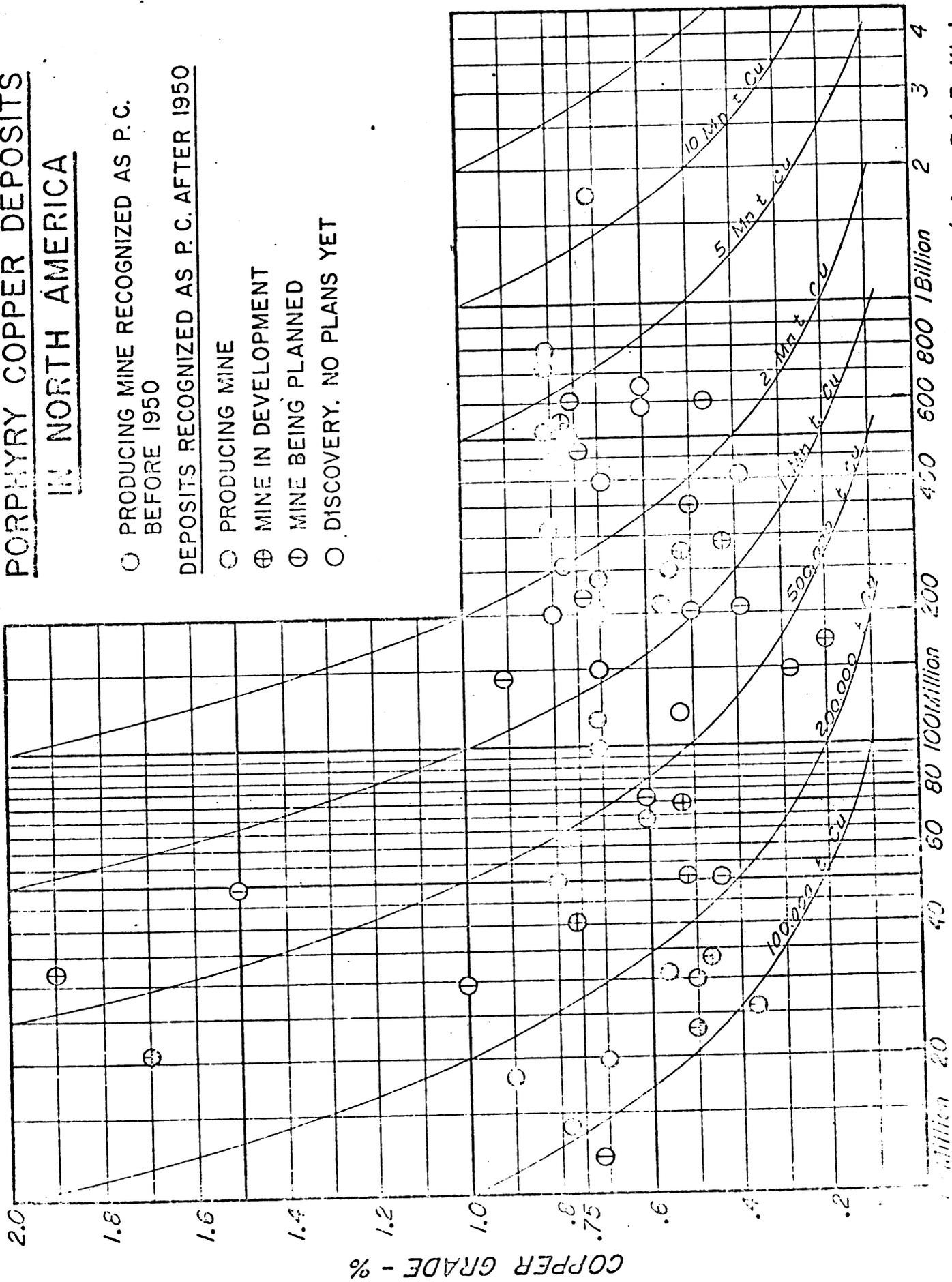
⊕ DEPOSITS RECOGNIZED AS P. C. AFTER 1950

○ PRODUCING MINE

⊕ MINE IN DEVELOPMENT

○ MINE BEING PLANNED

○ DISCOVERY. NO PLANS YET



"R. SERVES" TONNAGE AS OF 1971 IN SHORT TONS (after P.A. Bailly)

CLAY MINERAL STRUCTURES

~~2 octah~~ - open all sites - ~~Structure~~ - ~~all 2nd~~
~~2 octah~~ - ~~all sites~~ - ~~Structure~~ - ~~all 2nd~~
~~2 octah~~ - ~~all sites~~ - ~~Structure~~ - ~~all 2nd~~

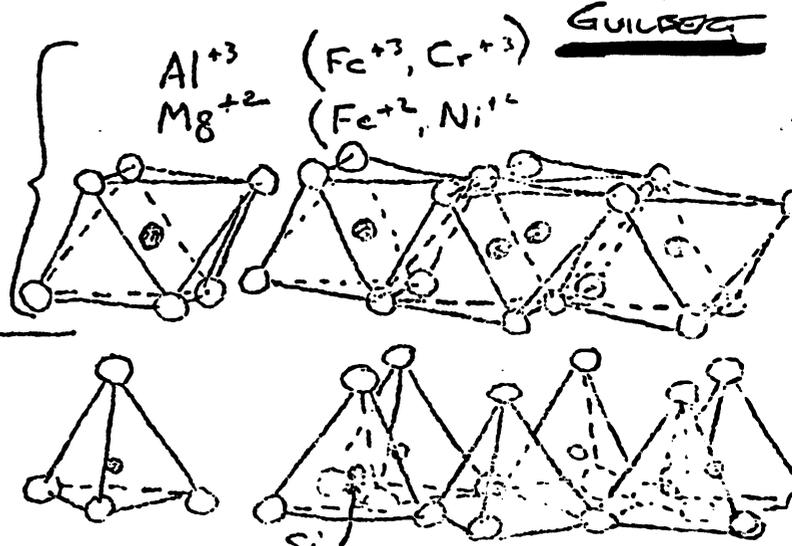
Decreases with K content
 ↓
 Ordovician
 sericite
 clay
 chlorite (very low)

GILBERT

GIBBSITE LAYER
 $Al_2(OH)_6$; $2/3$ SITE OCCUPANCY
 DIOCTAHEDRAL; CN 6

BRUCITE LAYER
 $Mg_3(OH)_6$; $2/3$ SITE OCCUPANCY
 TRIOCTAHEDRAL; CN 6

SILICA LAYER
 $Si_4O_6(OH)_4$
 TETRAHEDRAL; CN 4



KAOLINS 1:1 LATTICE STRUCTURE

GIBBSITE LAYER	$\left\{ \begin{array}{l} 6 OH^{1-} \\ 4 Al^{3+} \\ 4 O^{2-} + 2(OH)^- \end{array} \right.$	$\left\{ \begin{array}{l} Fe \text{ sub for Al} \rightarrow \text{Chamosite} \\ Mg \text{ sub for Al} \rightarrow \text{Trioc. An-} \\ \text{Gibbsite, } Mg_3Si_2O_5 \cdot 2H_2O \end{array} \right.$
SILICA LAYER		
	$\left\{ \begin{array}{l} 4 Si^{4+} \\ 6 O^{2-} \end{array} \right.$	$Al_4Si_4O_{10}(OH)_8$

MONTMORILLONITE S 2:1 LATTICE STRUCTURE

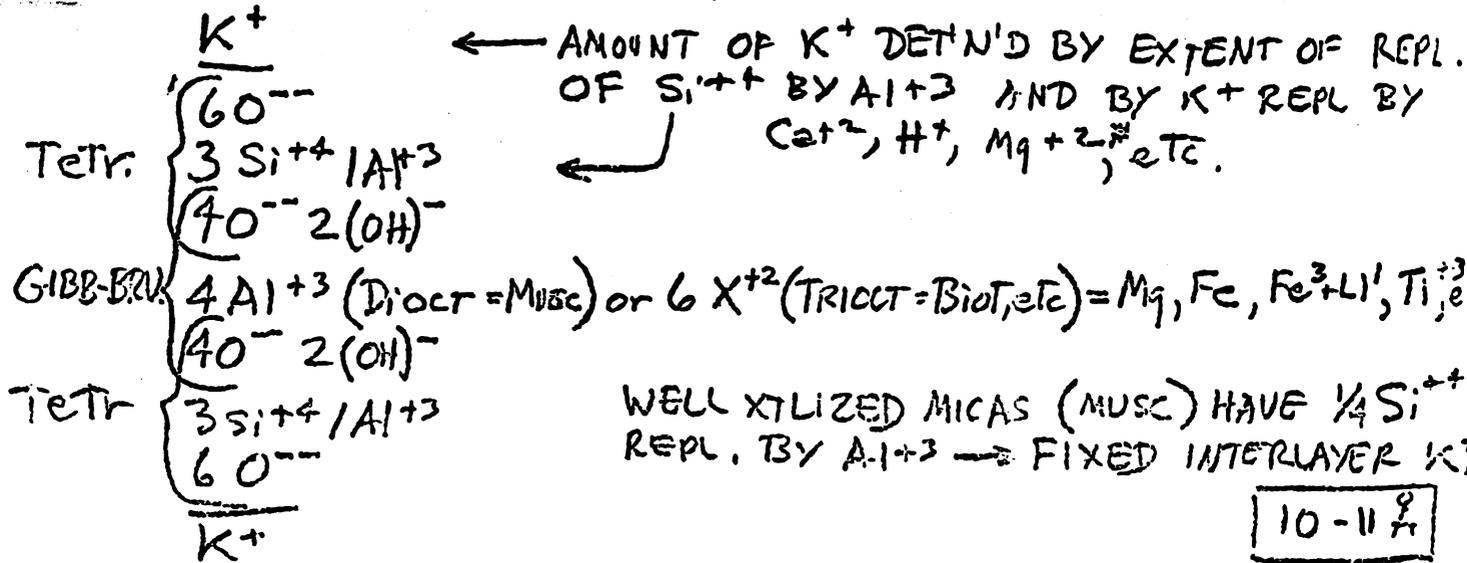
SILICA	$\left\{ \begin{array}{l} 6 O^{2-} \\ 4 Si^{4+} \\ 4 O^{2-} + 2(OH)^- \\ 4 Al^{3+} \\ 4 O^{2-} + 2(OH)^- \\ 4 Si^{4+} \\ 6 O^{2-} \end{array} \right.$	THEORETICAL (ONLY) FORMULA IS $(OH)_2 Si_2Al_4O_{20} \cdot nH_2O$
GIBBSITE BRUC.		← ALWAYS SOME Mg, Fe, Zn, Ni, Li
SILICA		← Al sub possible, poss also pits.

INTERLAYER LAYER OF WATER, ETC

Replacement of $2 Al^{3+}$ by $3 Mg^{+2}$ → SAPONITE
 " " $2 Al^{3+}$ " $2 Fe^{+2}$ → NONTRONITE
 " " $2 Al^{3+}$ " $2 Cr^{+3}$ → VOLKONSKOITE
 " " $2 Al^{3+}$ " $3 Zn^{+2}$ → SAUCONITE

GENERAL FORMULA FOR MONT = $[Al^{3+}Fe^{3+}Fe^{2+}Mg^{2+}]^I [Al^{3+}Si^{4+}]^{II} O_2(OH)^- + CATION^{2+}$

ILLITES 2:1 LATTICE STRUCTURE



CHLORITES 2:1 LATTICE STRUCTURE

* SAME BASIC STRUCTURE AS ILLITE, BUT WITH Mg(OH)₂ BETWEEN PACKETS = BOND. 14 Å
 CONSID. VARIATION IN Mg-Fe, Al-Si → LG NO. OF INDIVID. MINERALS, TRANSITIONAL PROPS

PYROPHYLLITE 2:1 LATTICE STRUCTURE

SIMILAR TO MUSC. OR MONT, BUT NO INTERLAYER ION. APPROACHES THEORETICAL MONT. FORMULA.
 $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$

ALLOPHANE

AMORPHOUS $\text{Al}_2\text{O}_3 \cdot m \text{SiO}_2 \cdot n \text{H}_2\text{O} \pm \text{Fe}_2\text{O}_3, \text{etc}$

ATTAPULGITE

Si Tetr. CHAINS RATHER THAN SHEETS
 PLYGORSKITE - MOUNTAIN LEATHER

TABLE 1. CLASSIFICATION OF THE CLAY MINERALS

Type	Group (x charge per formula unit)	Subgroup	Species*
1:1	Kaolinite-serpentine x ~ 0	Kaolinites Serpentines	Kaolinite, halloysite Chrysotile, lizardite, antigorite
2:1	Pyrophyllite-tale x ~ 0	Pyrophyllites Tales	Pyrophyllite Tale
2:1	Smectite or Montmorillonite- saponite x ~ 0.25-0.6	Diocahedral smectites or Montmorillonites Triocahedral smectites or Saponites	Montmorillonite, beidelite, nontronite Saponite, hectorite, sauconite
2:1	Vermiculite x ~ 0.6-0.9	Diocahedral vermiculites Triocahedral vermiculites	Diocahedral vermiculite Triocahedral vermiculite
2:1	Mica† x ~ 1	Diocahedral micas Triocahedral micas	Muscovite, paragonite Biotite, phlogopite
2:1	Brittle mica x ~ 2	Diocahedral brittle micas Triocahedral brittle micas	Margarite Clintonite
2:1:1	Chlorite x variable	Diocahedral chlorites 4-5 oct. cations per formula unit Triocahedral chlorites (5-6 oct. cations per formula unit)	Pennine, clinochlore, prochlorite

*Only a few examples are given

†The status of *Illite* (or *hydroxylite*), *sericite*, etc. must be left open at present because it is not clear whether or at what level they would enter the Table; many materials so designated may be interstratified.

After I. B. Day and others, 1968, p. 323.

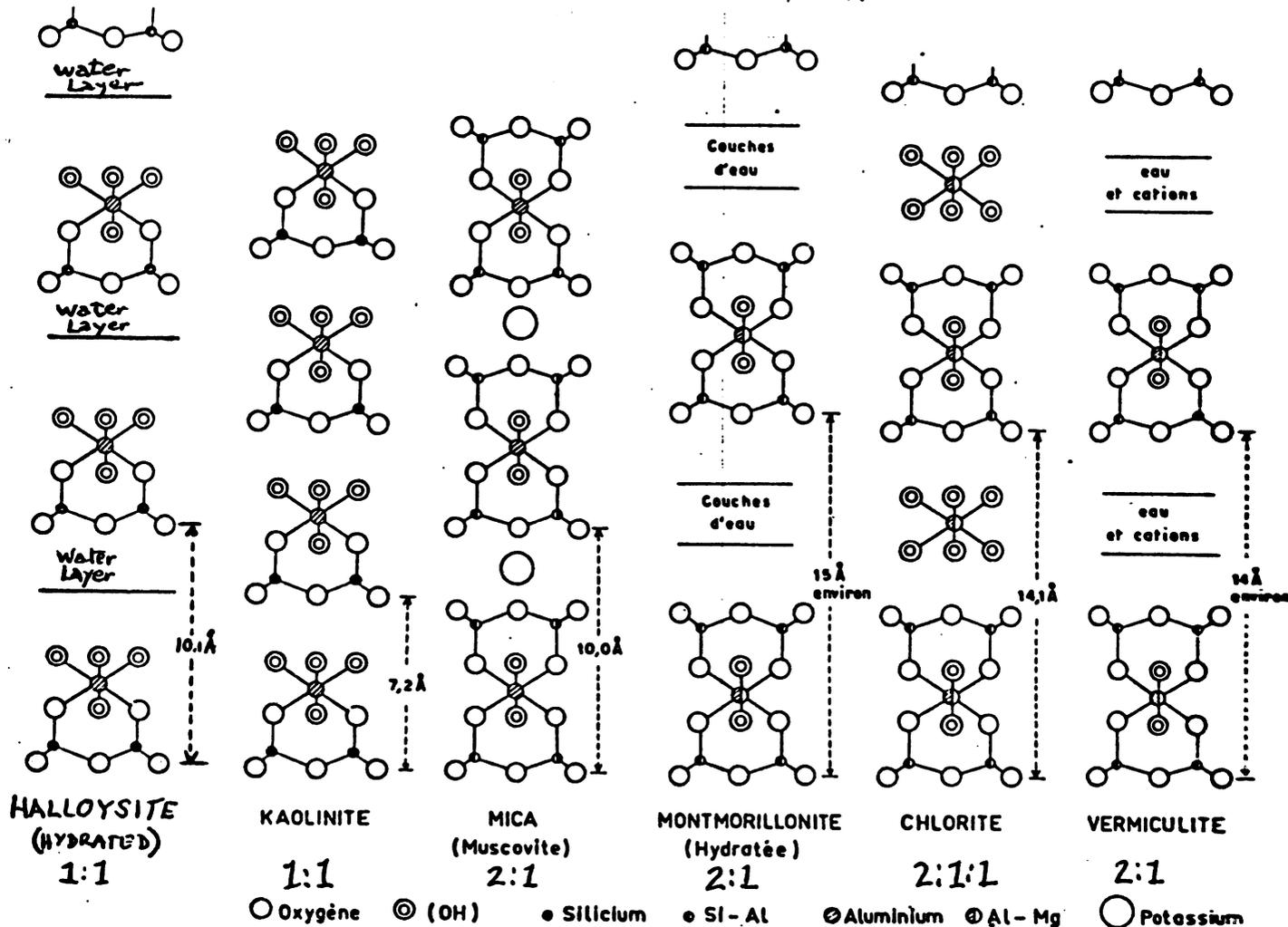
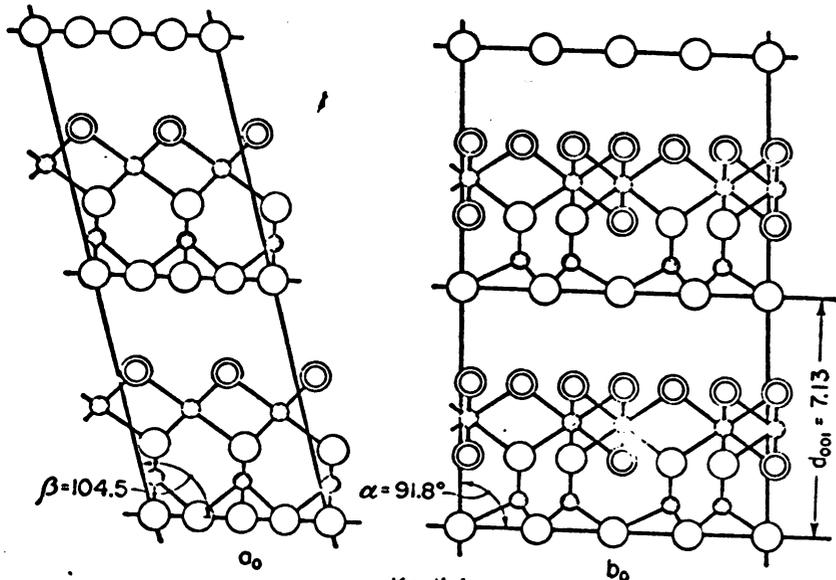


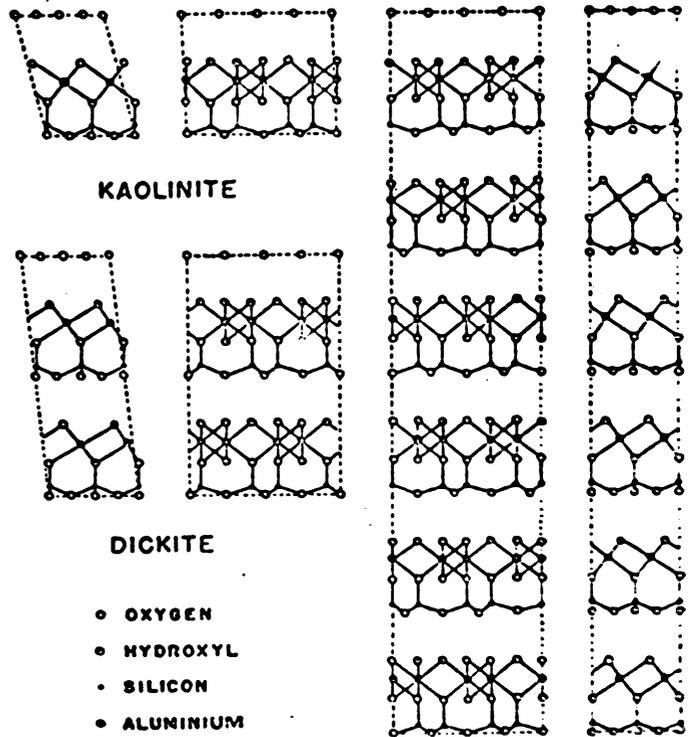
FIG. 1. — Représentation schématique de la structure des principaux minéraux phyllosilicés. (D'après BUNDEL, 1951.)



KAOLINITE

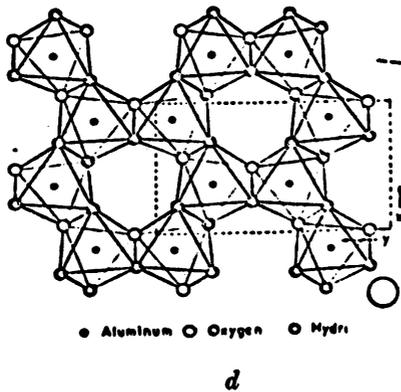
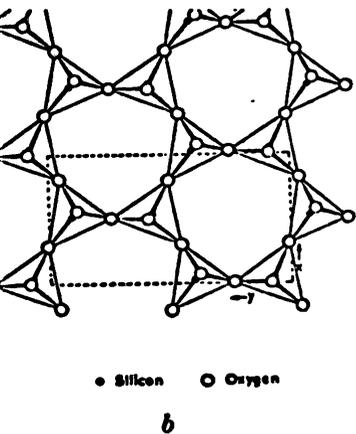
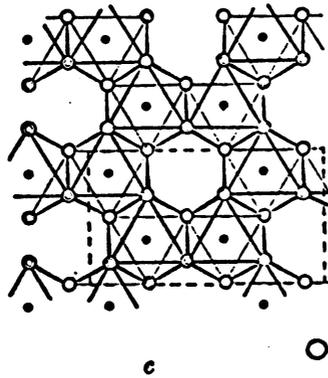
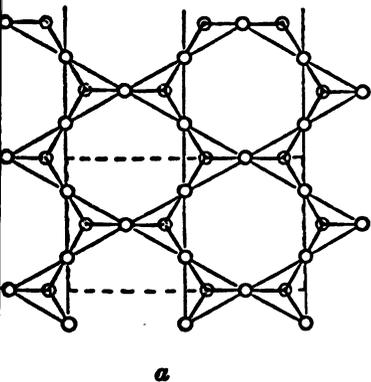


The stacking of unit layers of kaolinite along the *a* and *b* axes, after Brindley.

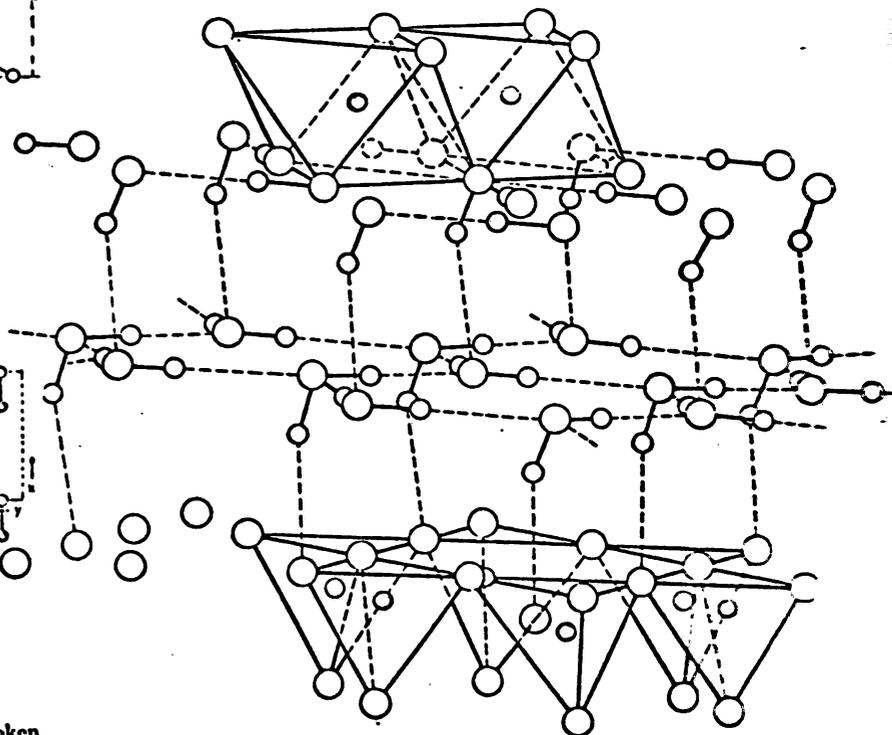


NACRITE

Comparison of the structures of kaolinite, dickite, and nacrite (after Newnham 1956).



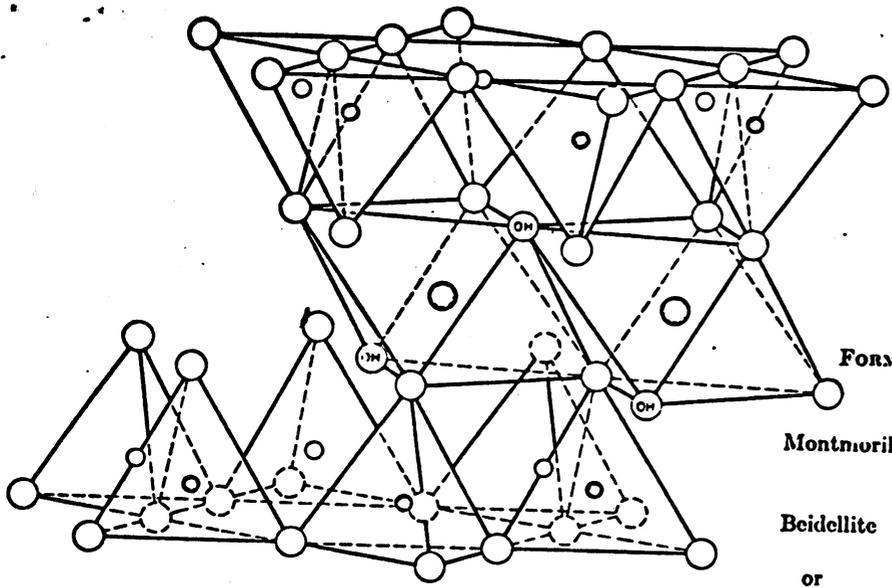
KAOLIN FAMILY



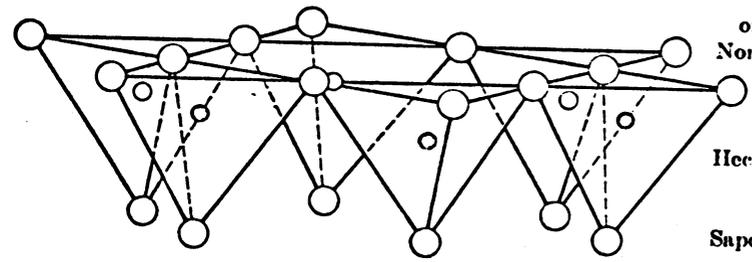
Tetrahedral and octahedral configurations in kaolin minerals. Broken lines show unit-cell boundary.

- (a) Ideal tetrahedral configuration.
- (b) Tetrahedral configuration obtained from the analysis of dickite.
- (c) Ideal octahedral configuration.
- (d) Octahedral configuration obtained from the analysis of dickite.

Diagrammatic sketch of a portion of the halloysite 4H-4 structure showing a single layer of water molecules with the configuration suggested by Hemmings and Jefferson.²²

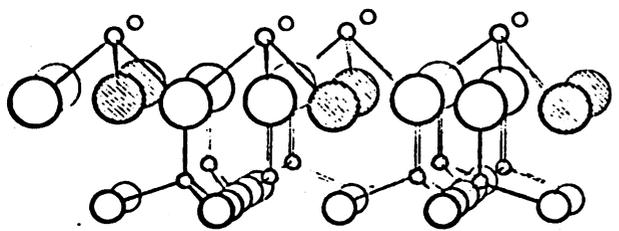


Exchangeable Cations
nH₂O

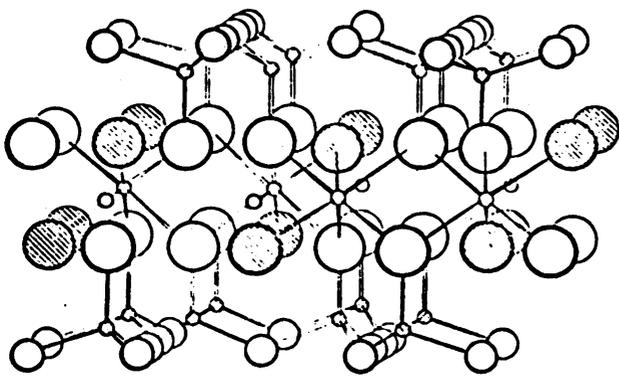


○ Oxygens ⊕ Hydroxyls ○ Aluminum, iron, magnesium
○ and ○ Silicon, occasionally aluminum

Diagrammatic sketch of the structure of montmorillonite according to Hofmann, Endell, and Wilm,²⁷ Marshall,²⁹ and Hendricks.¹⁸



4AlMg
4O₂OH
4Si
6O



6O
4Si
4O₂OH
4AlMg
4O₂OH



MONTMORILLONITES

FORMULAS FOR SOME MEMBERS OF THE MONTMORILLONITE GROUP SUGGESTED BY ROSS AND HENDRICKS³⁴

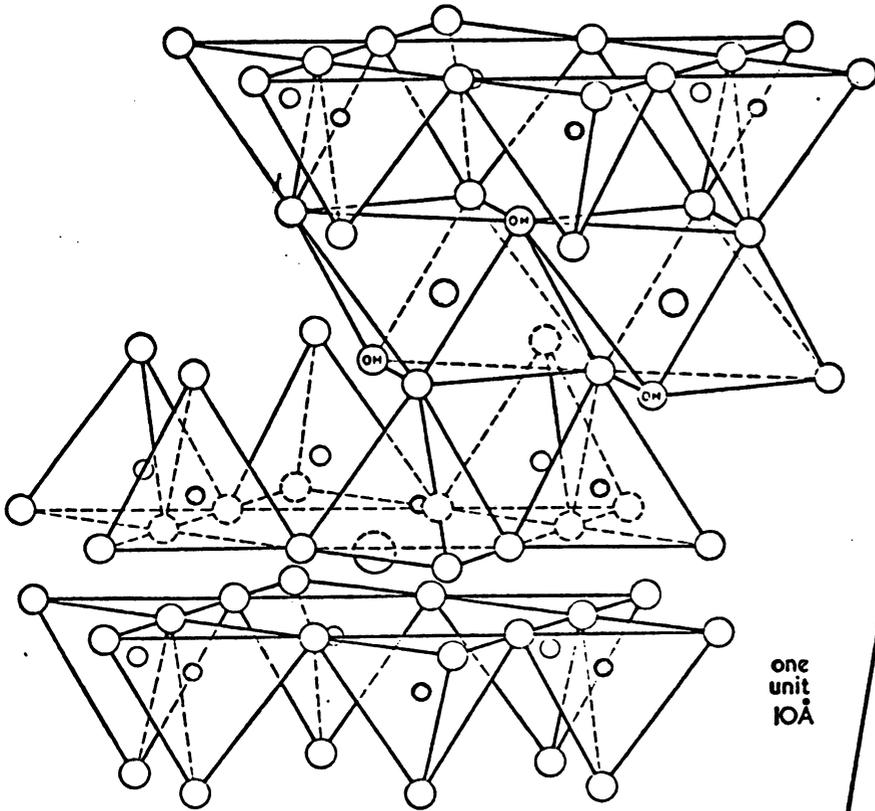
Diocahedral (heptaphyllitic) montmorillonites

- Montmorillonite $(OH)_4(Si_8(Al_{2.33}Mg_{.66})O_{20})$
- ↓ Na .66
- Beidellite $(OH)_4(Si_{6.33}Al_{1.66}Al_{1.33}O_{20})$
- ↓ Na .66
- or Beidellite $(OH)_4(Si_6Al_2)Al_{1.33}O_{20}$
- ↓ Na .66
- Nontronite $(OH)_4(Si_{7.33}Al_{.66}Fe_{1.33}^{2+}O_{20})$
- ↓ Na .66
- or Nontronite (aluminian) $(OH)_4(Si_{6.33}Al_{1.66}Fe_{1.33}^{2+}O_{20})$

Triocahedral (octaphyllitic) montmorillonites

- Hectorite $(OH)_4Si_8(Mg_{3.33}Li_{.66})O_{20}$
- ↓ Na .66
- Saponite $(OH)_4(Si_{7.33}Al_{.66})Mg_6O_{20}$
- ↓ Na .66
- or Saponite (aluminian) $(OH)_4(Si_{6.66}Al_{1.33})(Mg_{3.33}Al_{.66})O_{20}$
- ↓ Na .66

Structure of montmorillonite viewed along a axis (after Hofmann, Endell, Wilm, Macgdefrau, Marshall, and Hendricks). The layers are irregularly superposed. The magnesium content of montmorillonite varies from 1 to 3 per unit-cell layer (containing four six-coordinated ions). The octahedral sites are shown occupied in a regular way; the actual arrangement may be irregular. The large hatched circles represent hydroxyls. Figure modified from *Library and MacEwan (1953, Fig. 4).*

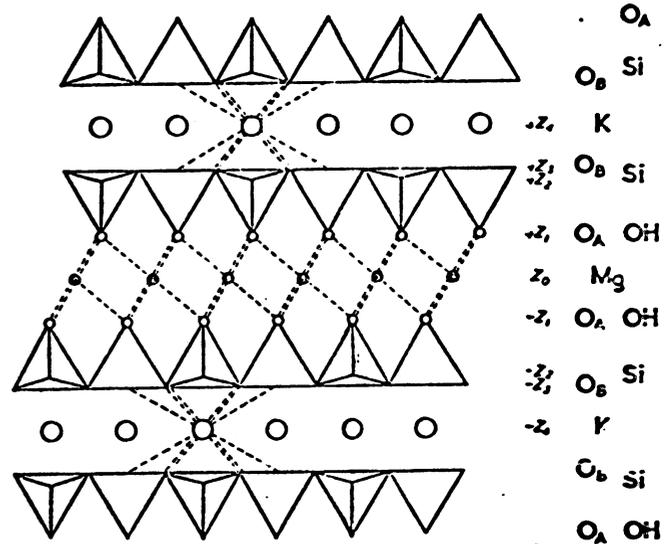


○ Oxygens, (OH) Hydroxyls, ○ Aluminum, ○ Potassium
○ and ○ Silicons (one fourth replaced by aluminums)

Diagrammatic sketch of the structure of muscovite.

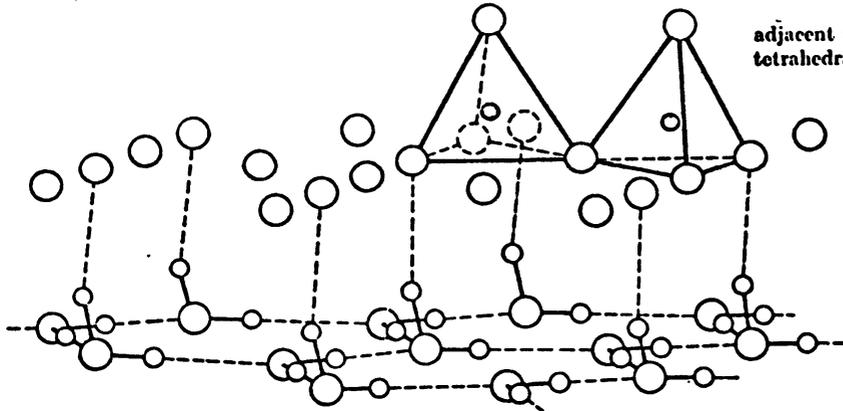
MUSCOVITE

PHLOGOPITE



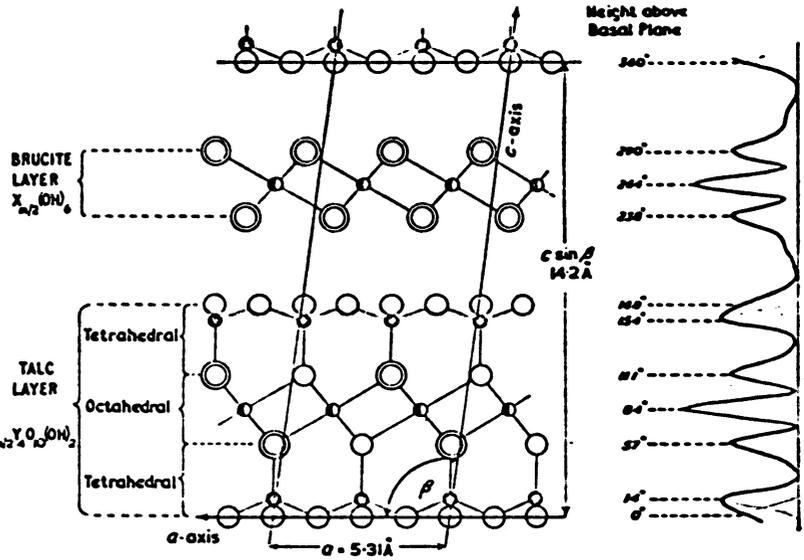
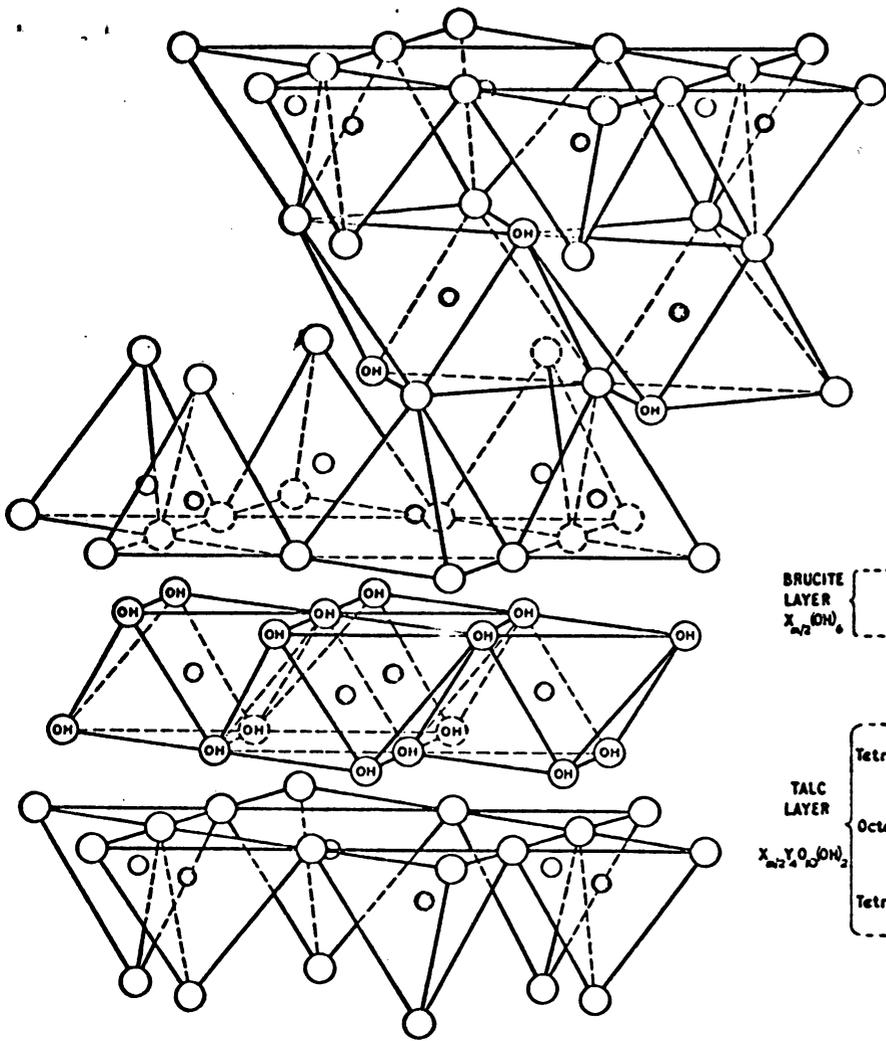
one unit
10Å

A projection on (010) showing one phlogopite layer, together with adjacent parts of the two adjoining layers. O_A and O_B are at the vertices of the tetrahedra. The O_A oxygens overlap with the OH ions (from Smith and Yoder 1956).



VERMICULITE

Diagrammatic sketch of the vermiculite structure showing layers of water, after Hendricks and Jefferson.⁵⁷



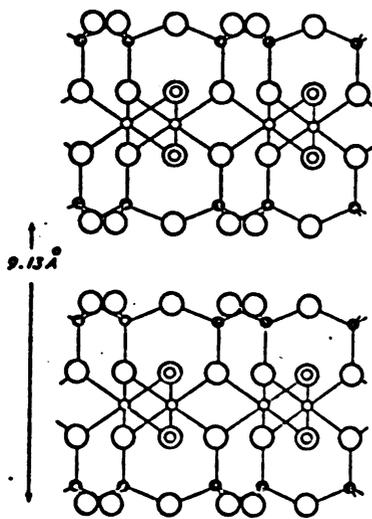
○ = Oxygen ⊙ = Hydroxyl ⊖ = X ⊙ = Y

Diagrammatic sketch of the structure of chlorite, after McMurchy.

Projection of the chlorite structure on the *ac* plane (after McMurchy) and a Fourier synthesis of electron density normal to the *ab* plane.

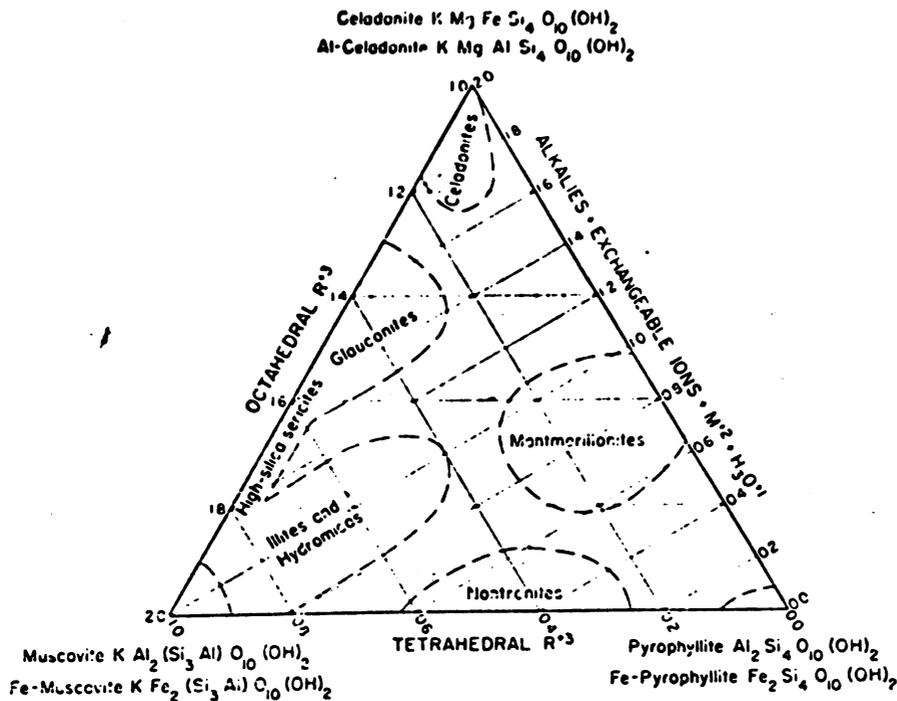
CHLORITE

PYROPHYLLITE

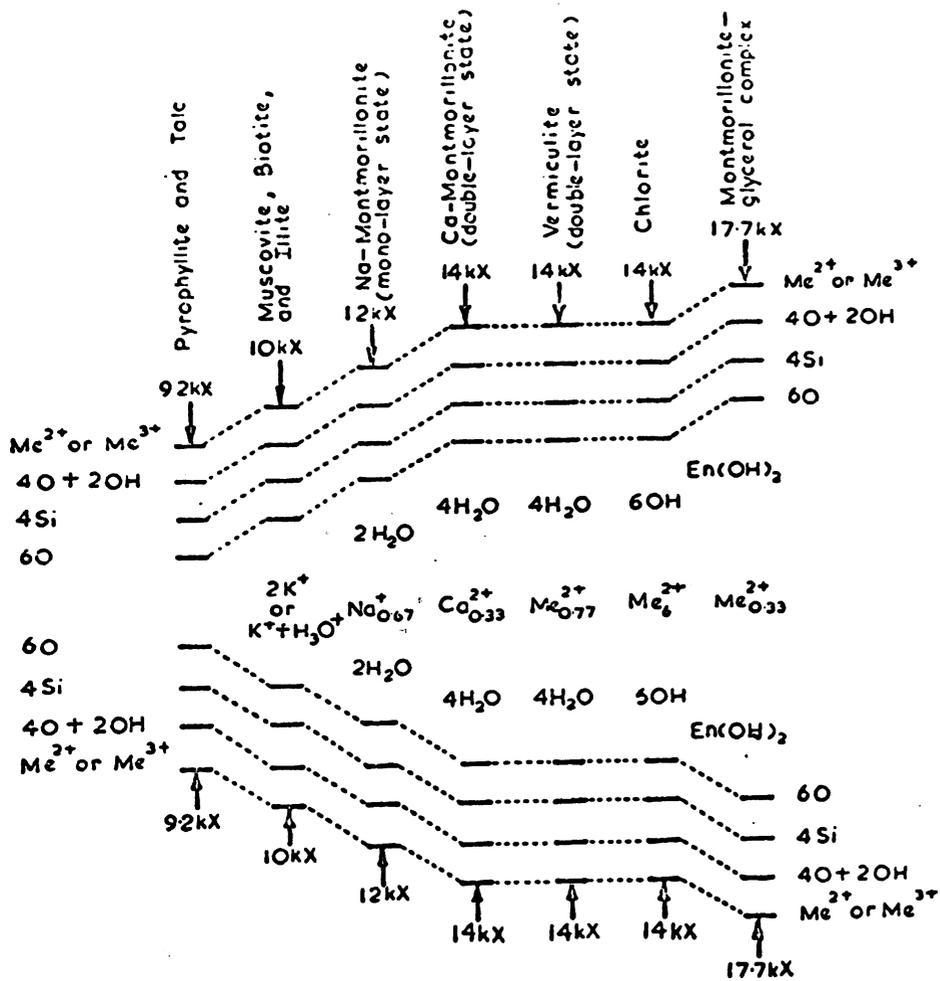


○ O ⊙ OH ⊙ Al ⊙ Si

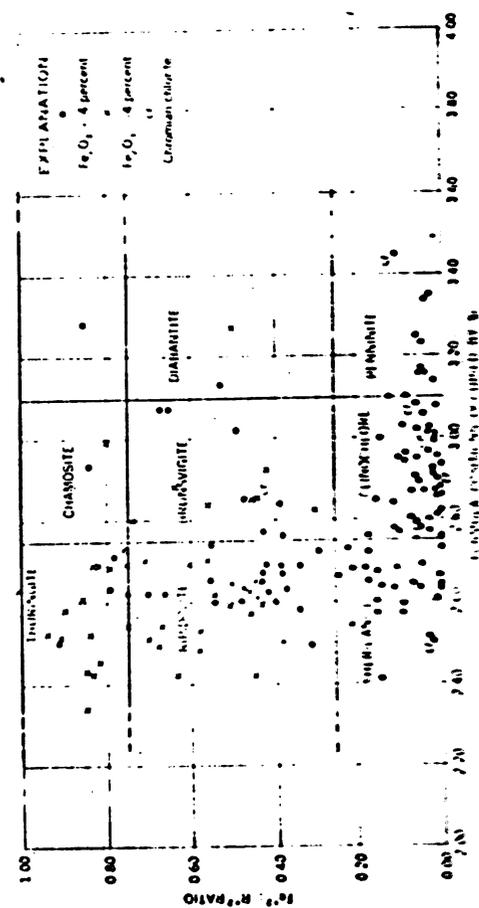
Structure of pyrophyllite (schematic) viewed along the *a* axis (from Edelman and Favejee 1940).



Mineralogical relations of members of the dioctahedral mica group (after Yoder and Eugster, 1955). Reprinted by courtesy of Pergamon Press, Inc.



Possible mixed-layering of clay minerals (after Cole and Hosking, 1957, p. 249). Reprinted by courtesy of the Mineralogical Society, London.



Classification of chlorites based on the two principal axes of ionic replacement (Foster, 1962, p. A19).

Table 30. SUMMARY OF THE PRINCIPAL CHARACTERISTICS OF THE CLAY MINERAL GROUPS

	Kandites	Illites	Smectites	Vermiculites
Structure type:	1:1 tetrahedral and octahedral components (diphormic)	2:1 (triphormic)	2:1 (triphormic)	2:1 (triphormic)
Octahedral component:	di-octahedral	mostly di-octahedral	di- or tri-octahedral	mostly tri-octahedral
Principal inter-layer cations:	nil	K	Ca, Na	Mg
Inter-layer water:	only in halloysite (one layer water mols.)	some in hydromuscovite	Ca, two layers; Na, one layer water mols.	two layers
Basal spacing:	7.1 Å (10 Å in halloysite)	10 Å	variable; most ≈ 15 Å (for Ca)	variable; 14.5 Å when fully hydrated
Glycol:	taken up by halloysite only	no effect	takes two layers glycol, 17 Å	takes one layer glycol, 14 Å
Chem. formula:	$Al_2Si_4O_{10}(OH)_2$, little variation	$K_{1-0.5}Al_2(Si,Al)_4O_{10}(OH)_2$	$M^{+0.66}(Y^{++}, Y^{+})_{4-4}(Si,Al)_4O_{10}(OH)_2nH_2O$	$M^{+2.0}(Y^{++}, Y^{+})_2(Si,Al)_4O_{10}(OH)_2nH_2O$
Acids:	kaolinite scarcely soluble in dil. acids	readily attacked	attacked	readily attacked
Heating 200°C.	halloysite collapsed to 7.4 Å, others unchanged	no marked change	collapse to approx. 10 Å	exfoliation; shrinkage of layer spacing
Heating 650°C.	kaolinite → meta-kaolinite 7 Å dickite → meta-dickite strong 14 Å	10 Å	9.6-10 Å	collapse to 9 Å of talc
Optics α	1.55-1.56	1.54-1.57	1.48-1.51	1.52-1.57
γ	1.56-1.57	1.57-1.61	1.50-1.53	1.54-1.58
δ	≈ 0.006	≈ 0.03	0.01-0.02	0.02-0.03
2V	24°-50°	< 10°	variable	< 10°
Paragenesis:	alteration of acid rocks, feldspars, etc. Acidic conditions	alteration of micas, feldspars, etc. Alkaline conditions. High Al and K concentrations favourable	alteration of basic rocks, volcanic material. Alkaline conditions. Availability of Mg and Ca, deficiency of K	alteration of biotite flakes or of volcanic material, chlorites, hornblende, etc.

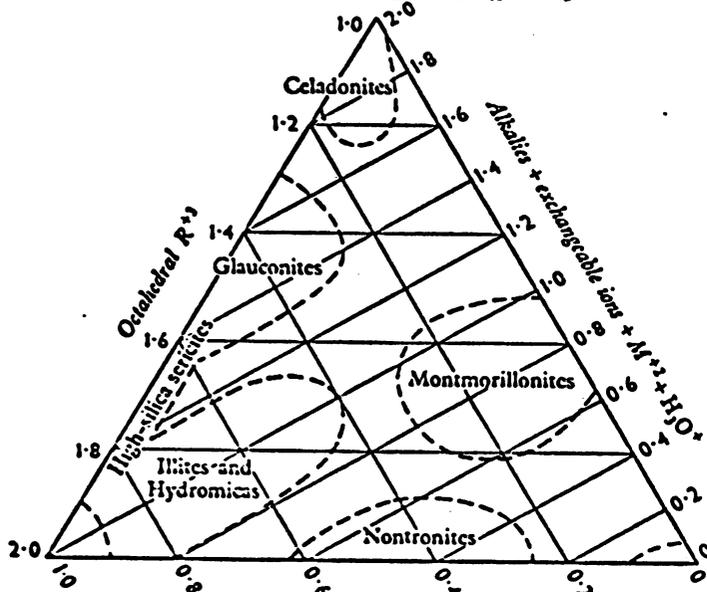
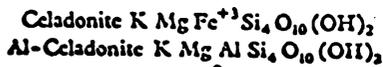


FIG. 49. Plot of tetrahedral R^{3+} and octahedral R^{3+} in atomic proportions, for di-octahedral micas and related minerals (after Yoder and Eugster, 1955).

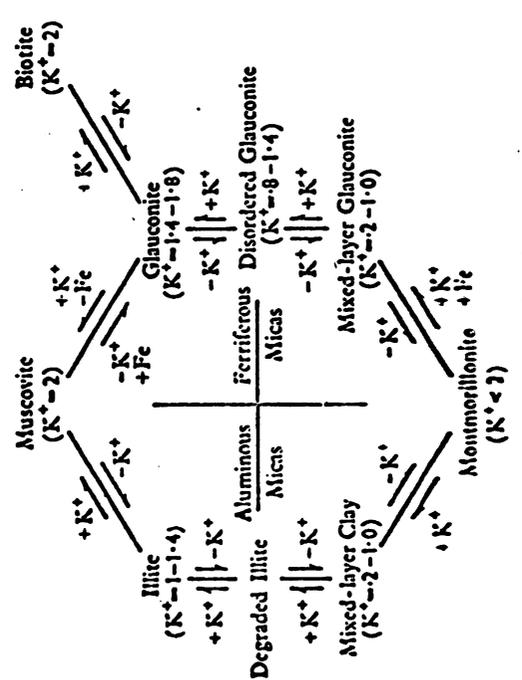


FIG. 50. The relation of glauconites to other micas and clay minerals (after Hurst, 1958).
K⁺ numbers = Potassium ions per formula unit

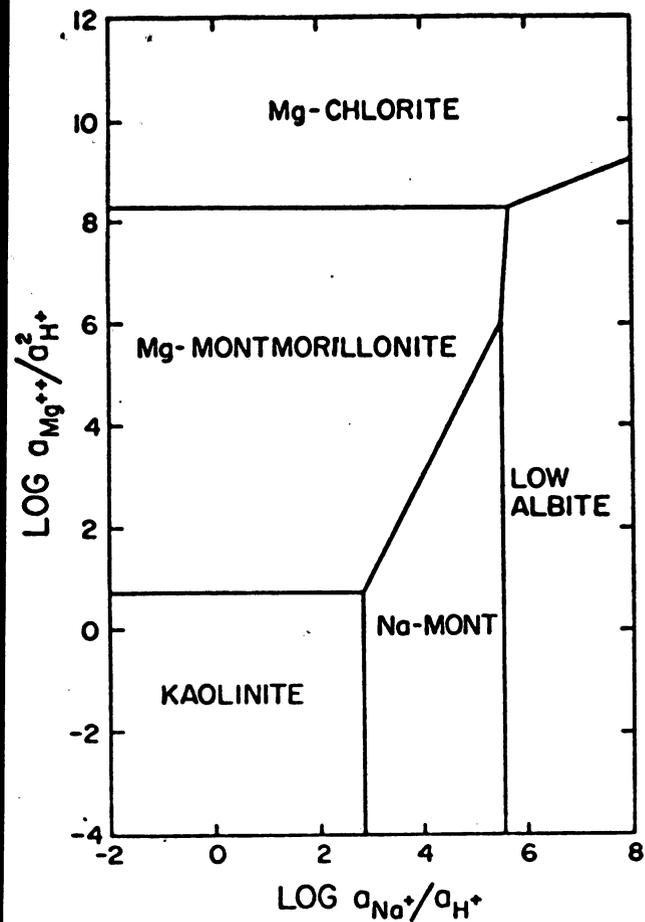


FIG. 5. Abridged theoretical activity diagram for the system $MgCl_2-NaCl-HCl-Al_2O_3-SiO_2-H_2O$ in the presence of quartz and an aqueous phase at $200^\circ C$, one atmosphere, and unit activity of H_2O (Helgeson, Brown, and Leeper, 1969—reproduced with permission from Freeman, Cooper and Co.).

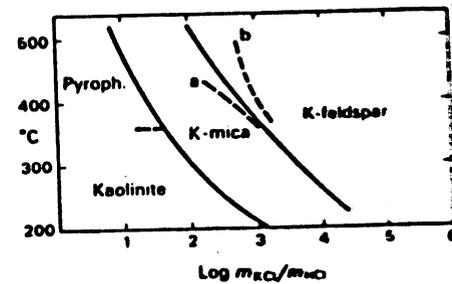
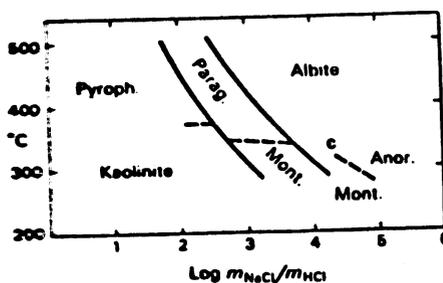
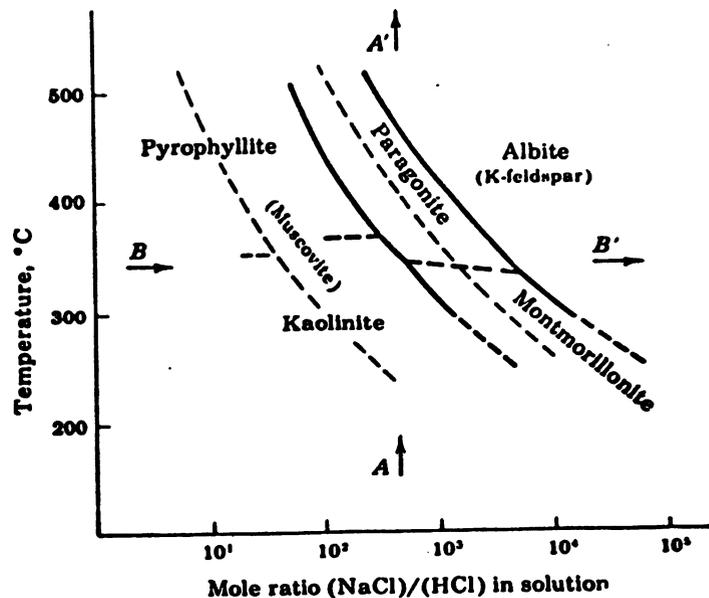
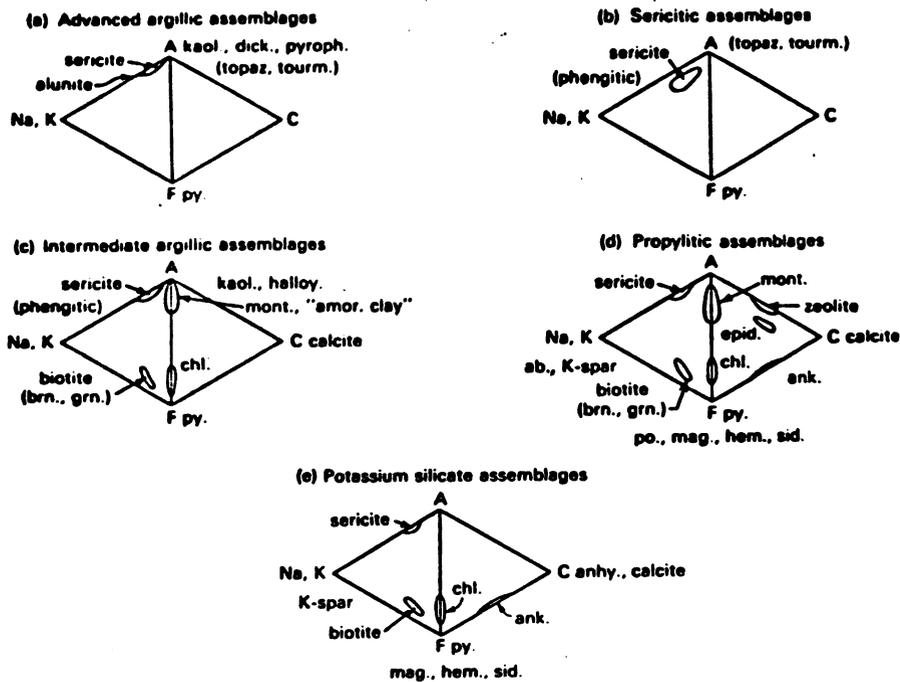


FIG. 6.5. Some equilibrium relations in the systems $Na_2O-Al_2O_3-SiO_2-H_2O$ (above) and $K_2O-Al_2O_3-SiO_2-H_2O$ (below) in a chloride electrolyte environment. Total pressure is 15,000 psi and quartz is present. Dashed curves: a, K-feldspar-mica equilibrium at 5000 psi; b, at 30,000 psi; c, segment of decomposition curve of anorthite to calcium montmorillonite in calcium chloride solutions.

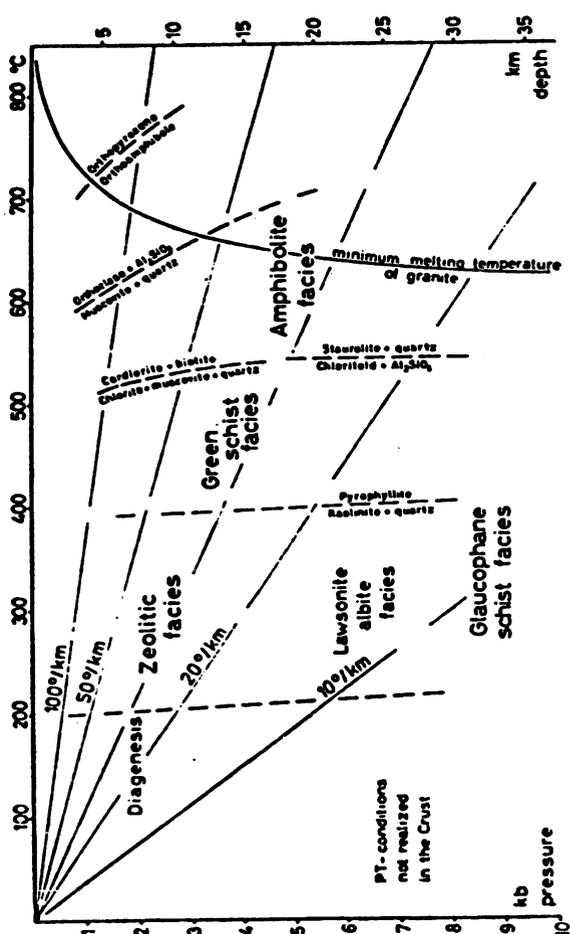


Fig. 9-1. Distribution of mineral facies in a temperature-pressure diagram of the upper crust according to WINKLER (1967)

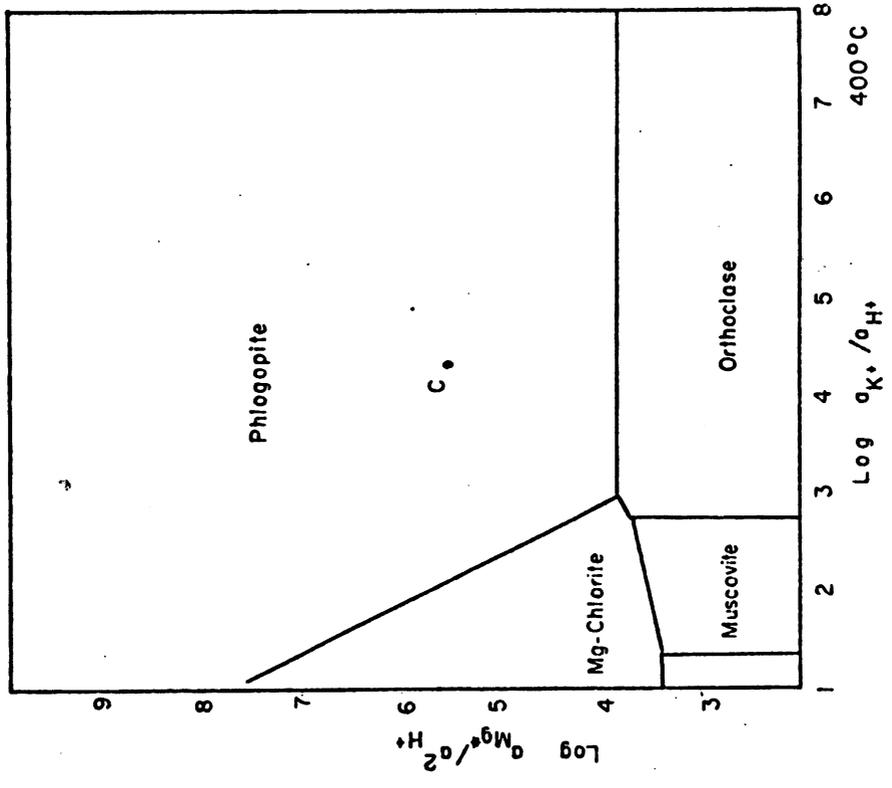
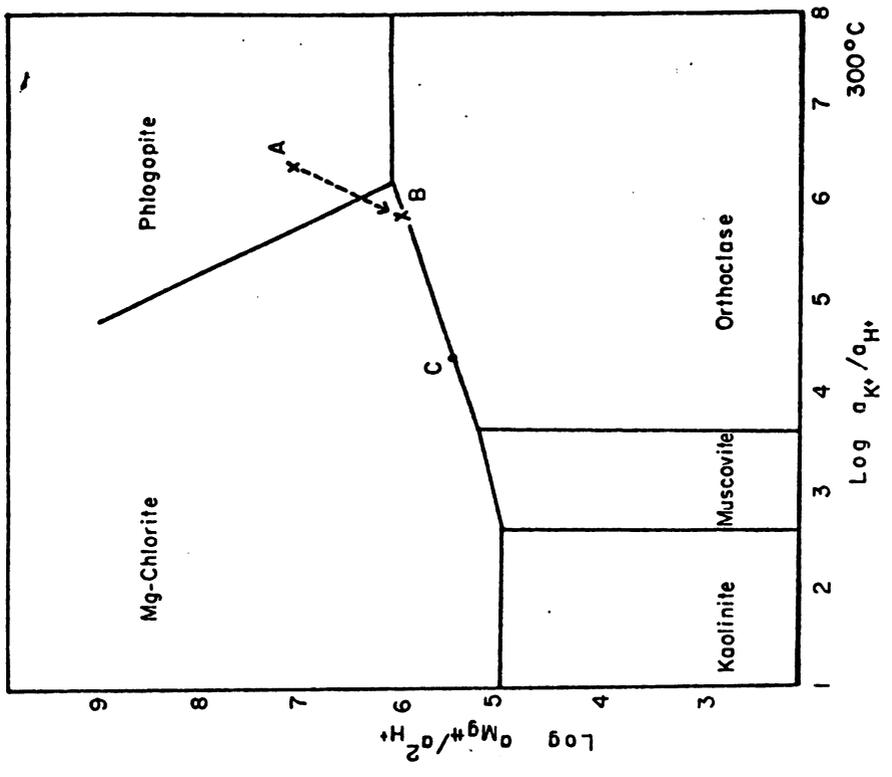
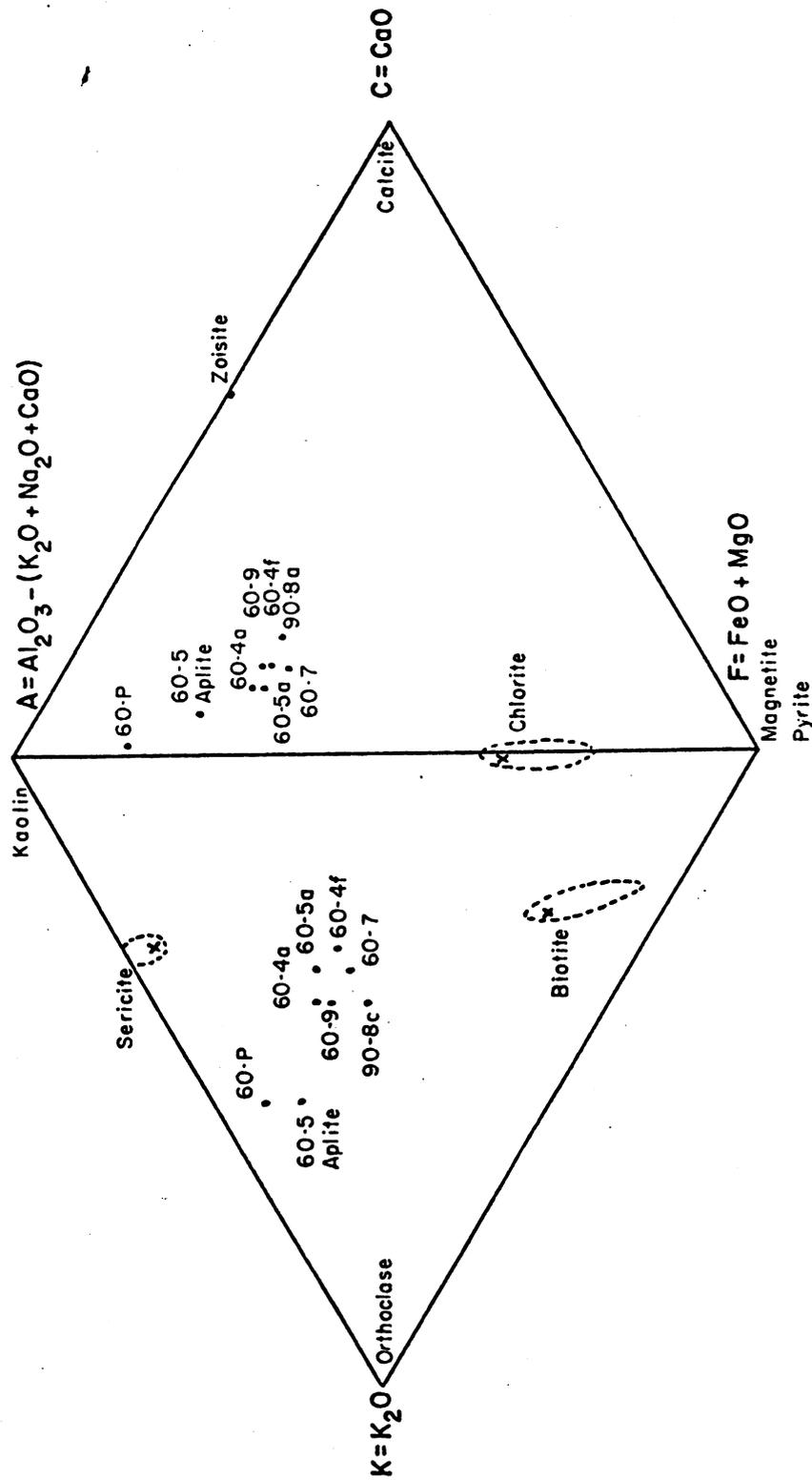
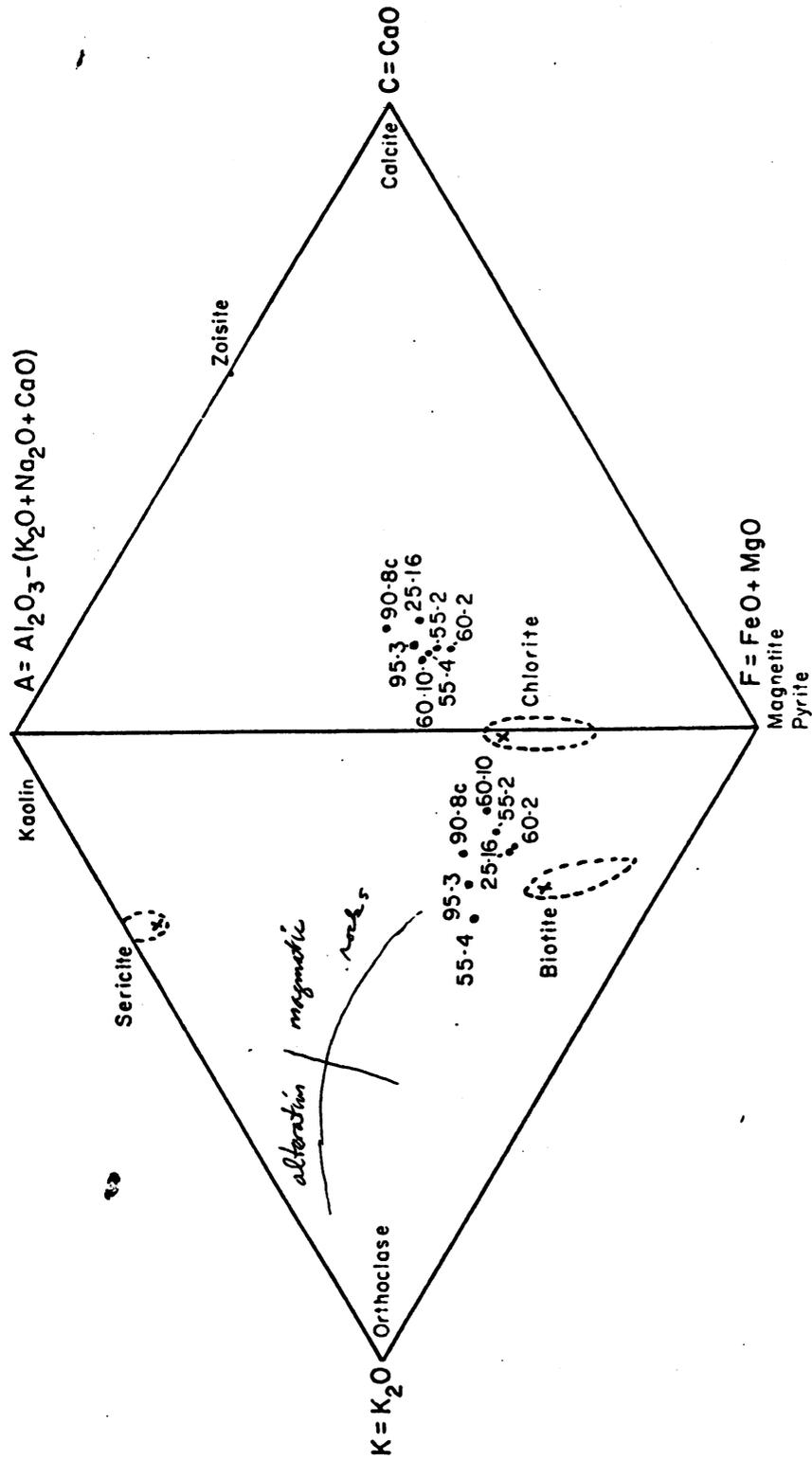


Figure 53. $\text{Log } a_{\text{Mg}^{++}/a_{\text{H}^+}^2}$ versus $\text{Log } a_{\text{K}^+}/a_{\text{H}^+}$ diagrams for 300 and 400°C.



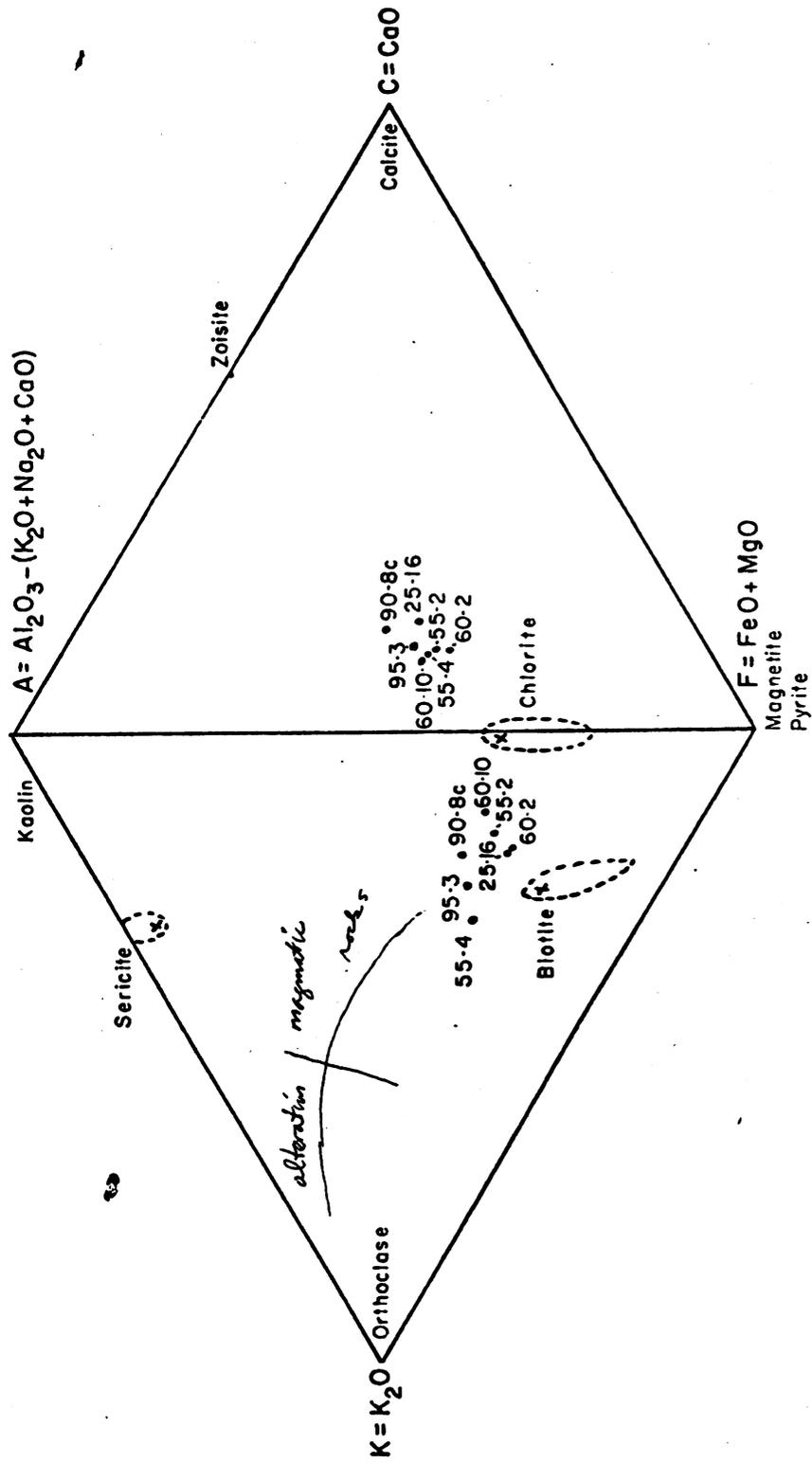
x = plot of analyzed Individual Esperanza minerals (Tables 7 and 8)

Figure 42. Combined AKF-ACF diagram for quartz monzonite porphyry, aplite, and orthoclase metasomatite samples from Esperanza.



x = plot of analyzed individual Esperanza minerals (Tables 7 and 8)

Figure 44. Combined AKF-ACF diagram for biotite quartz diorite samples from Esperanza.



x = plot of analyzed individual Esperanza minerals (Tables 7 and 8)

Figure 44. Combined AKF-ACF diagram for biotite quartz diorite samples from Esperanza.

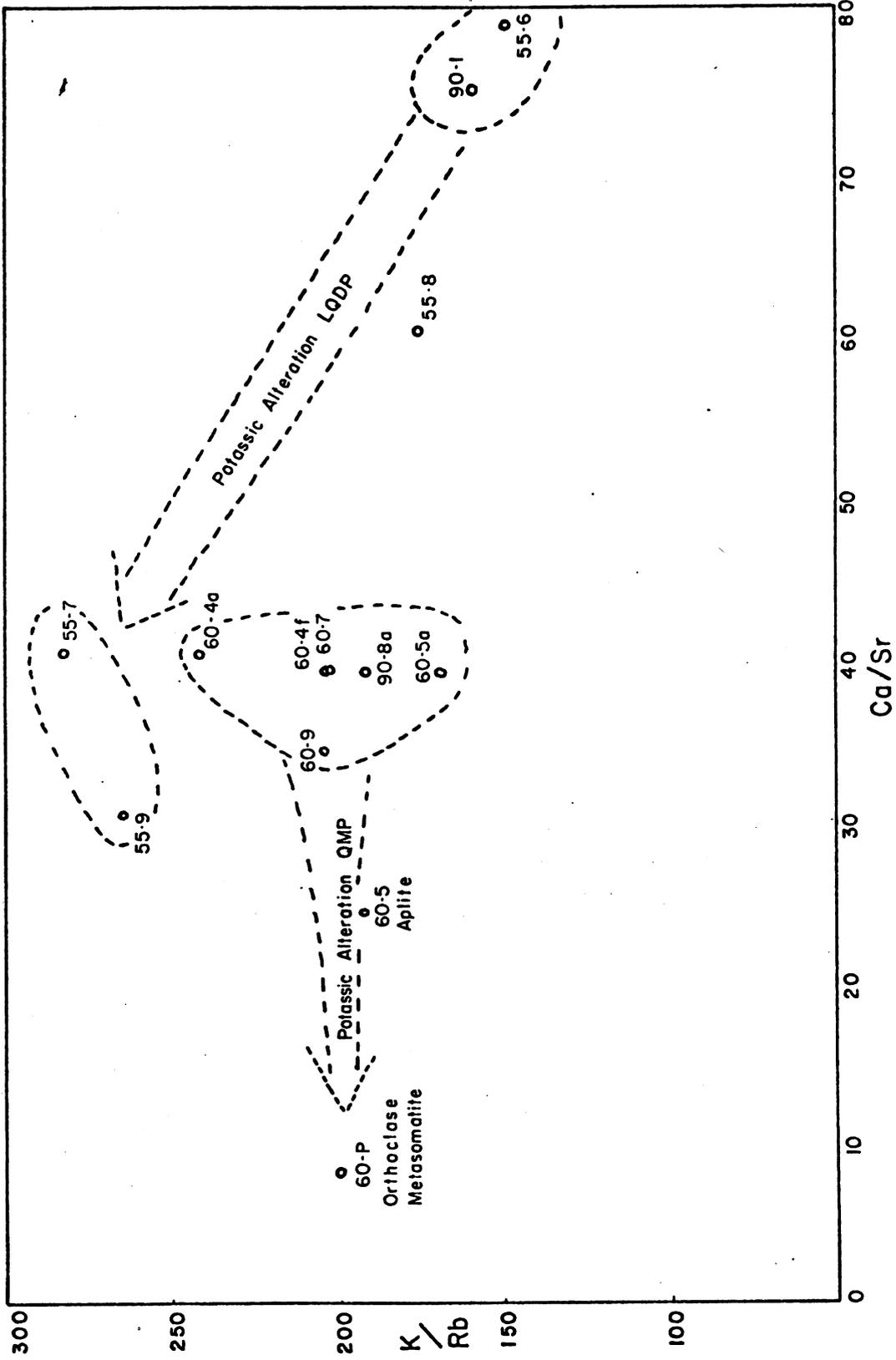


Figure 48. K/Rb vs. Ca/Sr plot for quartz monzonite porphyry and leuco-quartz diorite porphyry.

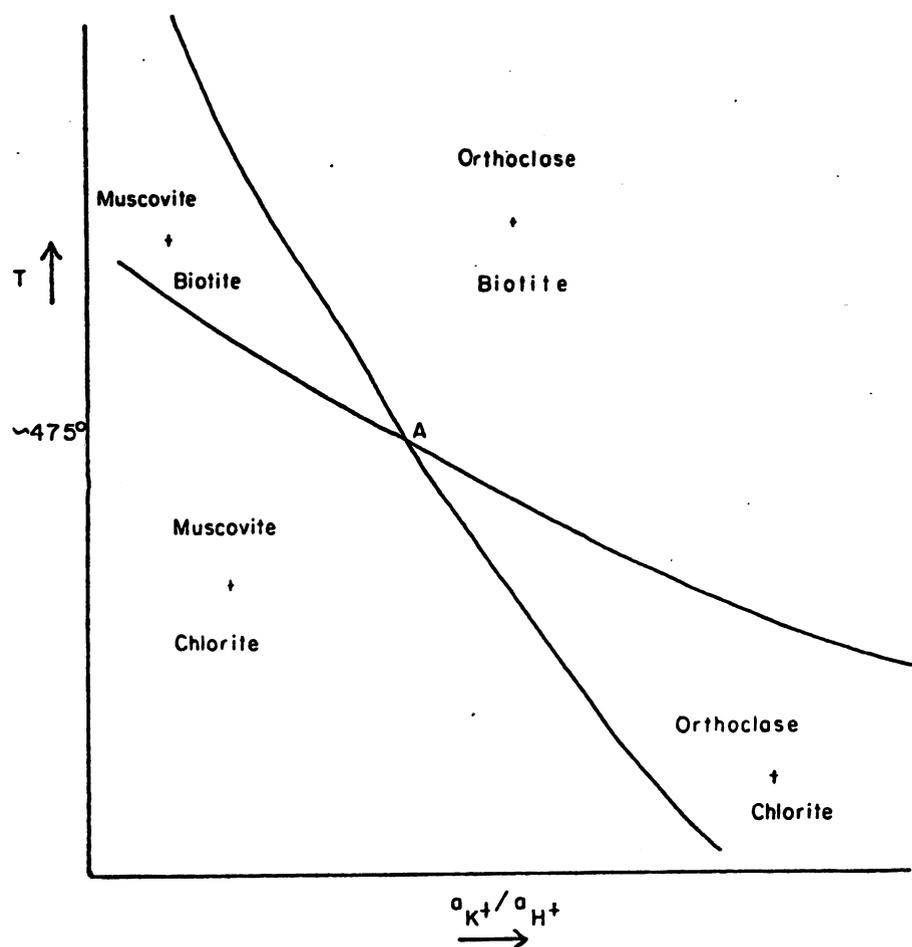


Figure 52. Schematic diagram of the system biotite-orthoclase-muscovite-chlorite-K-H₂O.

Modified from MacNamara (1966). Conditions: constant pressure and excess quartz.

Point A corresponds to the upper limit of stability of the orthoclase-chlorite assemblage at approximately 450-500°C (Hemley and Montoya, 1971, and Hoschek, 1973).

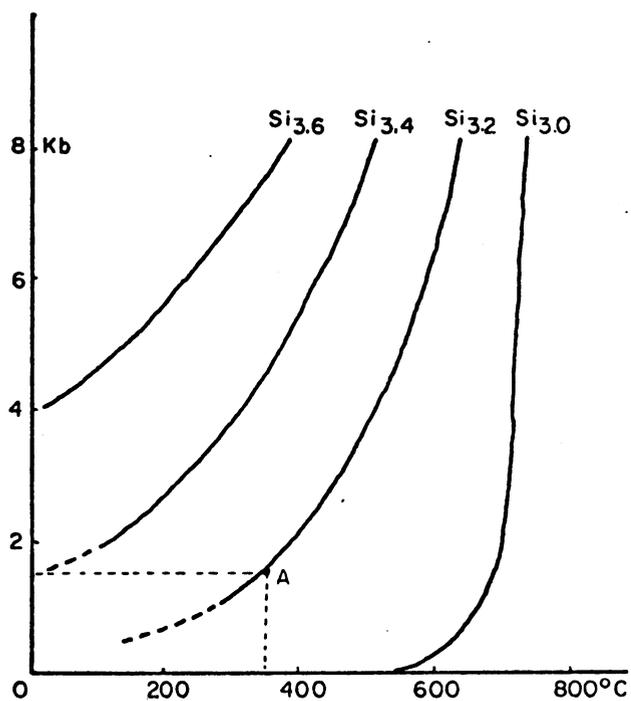


Figure 50. Stability curves for sericites.

From Velde (1967). Point A gives the Si⁴⁺ content of Esperanza sericites and the temperature and pressure data of Denis (1974).

PORPHYRY COPPER DEPOSITS

Variations in Zoning Patterns In Porphyry Ore Deposits

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**J. David Lowell, Consulting Geologist,
Tucson, Arizona**

Manuscript Submitted: on April 30, 1973; revised manuscript received November 16, 1973.

Keywords: Porphyry copper deposits, Zoning patterns, Alteration, Mineralization, Valley Copper deposit, JA deposit, Bethlehem Copper deposits, Marcopper deposit, Atlas deposit, Ajo deposit.



(Reprinted from The Canadian Mining and Metallurgical Bulletin, February, 1974)

Printed in Canada

OUTLINE OF DISCUSSION OF METASOMATISM
IN PORPHYRY COPPER DEPOSITS

Introduction

Paper will be concerned largely with field relations, geometry of rock units, and examination of rock specimens rather than with an analysis of geochemistry and phase diagrams, etc. . Papers by Stringham, Kirkham and Mauger will be very briefly reviewed.

Characteristics of Porphyry Copper Intrusions

- Granular or porphyritic igneous texture.
- Lack chilled margins & flow textures.
- Lack drag effects & wall rock deformation.
- Extensive wall rock alteration.
- "Passive emplacement" definition.
- Universal presence of certain igneous rock types and mineral assemblages.
- Theories of origin.

Zoning Evidence which Suggests Metasomatism

- San Manuel-Kalamazoo section: magmatic and hydrothermal environments overlap in space.
- Hemley-Jones phase diagram: magmatic vs. hydrothermal conditions defined.

Stringham work at Bingham

- Silica build up in sediments near stock.
- Evidence of passive emplacement.
- Comparison with Lowell-Guilbert tabulation of passive intrusions.

Evidence of metasomatism in other deposits.

- Fourmier quartzite bed at Ely.
- Aplite at Sierrita.
- Quartzite at Vekol.
- Scarn effects at Santa Rita, Morenci, Mission, Silver Bell, Ely, Yerrington, Carr Fork, etc..

Intermineral Dikes

- Examples from Granisle (Kirkham).
- Indicate overlap in time of magmatic and hydrothermal conditions.
- Analogy with Climax "nested cones" etc..
- Tawi-Tawi intermineral dike composition and wall rock zoning.
- Suggestion of overlap in both space and time of magmatic and hydrothermal conditions.

OUTLINE OF TALK ON STRUCTURAL AND ALTERATIONS SETTINGS
OF PORPHYRY COPPER SYSTEMS

Talk will be a broad review of porphyry districts of the world comparing the similarities and differences in the settings of the deposits. It will be a travelog presentation, to some extent, with a lot of slides and a number of suites of rock specimens from representative deposits. The talk will not involve a detailed discussion of geochemistry or petrography.

INTRODUCTION

Description of porphyry copper deposits

Physical Characteristics.

Distribution.

Variation of district characteristics with respect to (1) age, (2) size and grade, (3) physiographic and climatic setting, (4) wall rocks, (5) alteration, (6) structural controls, (7) geologic history and depth of erosion of original column of mineralization.

Specific features of southwest porphyry province

Setting: cluster-belt combined control.

Laramide epoch.

Basin-Range structure & NE extension.

Characteristics of deposits: mostly intermediate wall rocks, etc.

Post-mineral physiographic history and range of vertical exposure resulting from erosion and tilting.

Comments regarding plate tectonics

Coincidence of porphyry districts and mobile belts.

Ocean trenches and subduction zones reasonable hypothesis in Pacific.

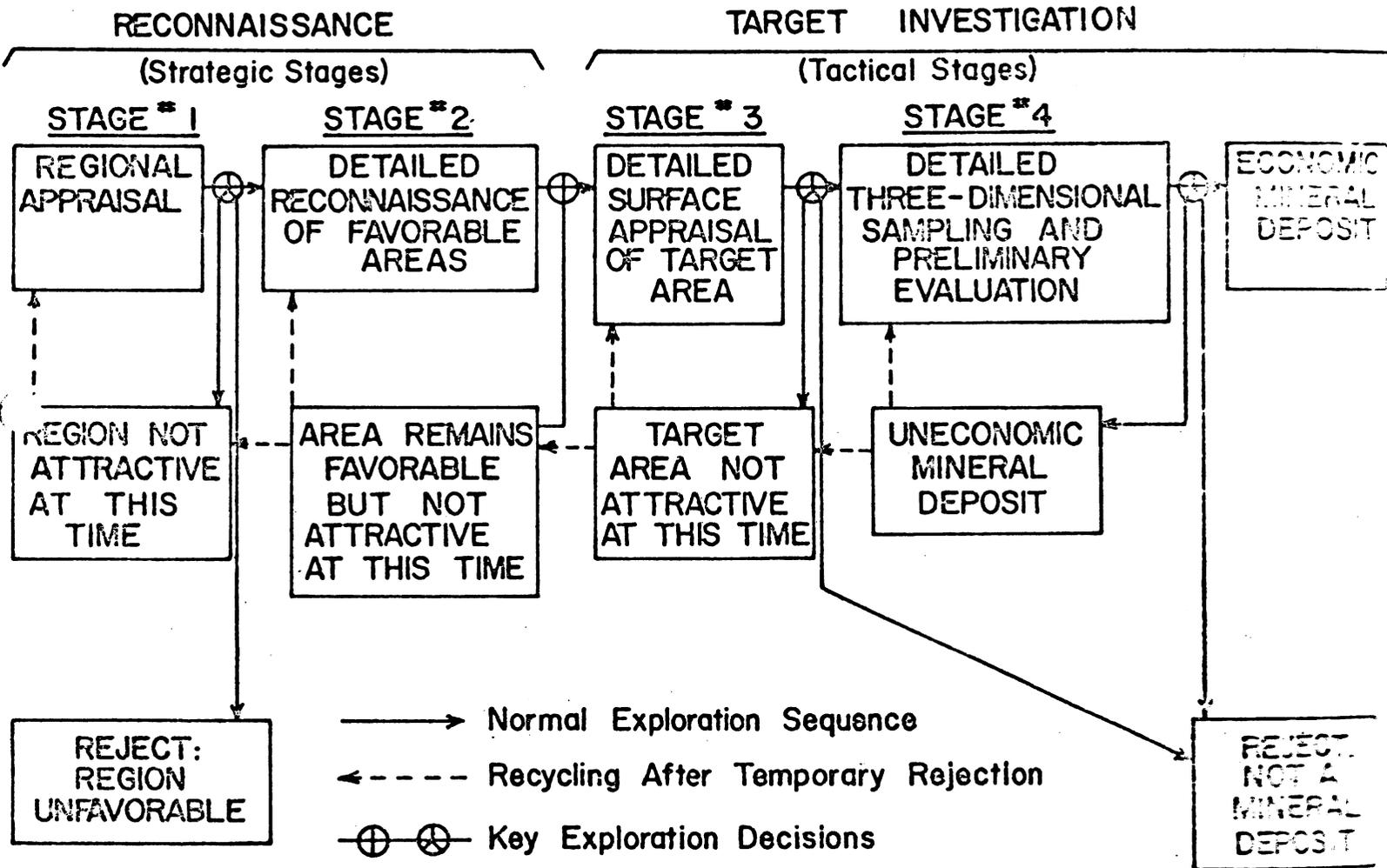
Discrepancies in South America and N. America settings.

Evidence in several porphyry copper districts of continued ore control in the same local area throughout geologic history resulting from either a persistent deep-seated feeder or from a heritage succession of ore deposition.

RICHARD

[I-P- 450-500
max

concept was FLAT FAULTS - young
CENOZOIC - MESOZOIC
EXOTIC DEPOSIT



MAIN ACTIVITIES AND METHODS EMPLOYED DURING THE FOUR STAGES OF EXPLORATION!

Search for a New Porphyry Copper Ore Deposit in Southwest U.S.A.

O, OFFICE STUDY:
 F, FIELD INVESTIGATION:
 L, LABORATORY TESTS:
 *INDISPENSABLE ACTIVITY OR METHOD

Stage 1--Regional Appraisal	Stage 2--Detailed Reconnaissance	Stage 3--Detailed Surface Investigation of Target Area	Stage 4--Detailed Three-Dimensional Physical Sampling of Target Area
O-Geologic Compilation* O-Photogeologic study (rock units and structure)? O-Structural analysis* F-Field inspection of area selected from air and/or ground*	F-Reconnaissance geologic mapping of outcrops* F-Stream-sediment geochemical surveys F-Aeromagnetic survey? F-Gravity survey in gravel-covered areas F-Reconnaissance induced polarization survey of covered areas?	F-Detailed geologic* --structural-alteration mapping of outcrops L-Petrographic-mineralogy trace element study of rock samples? F-Detailed induced polarization survey of anomalous covered areas	F-Drilling*-logging*, etc.? L-Mineralogical, chemical analyses and physical tests on samples, cores and cuttings* O-Reserves computation* O-Preliminary valuation* F-Investigation of water problems and water availability for plants* F-Shaft-sinking or tunneling to obtain bulk samples? L-Ore-dressing bulk tests

!After Bailly (modified), Surface Mining, Pfleider, E. P., ed., AIME, New York, 1968.

METHODS AND TECHNIQUES	Useable at Stages				Detection* Capability for Non-Ferrous Metallic Deposits			
	#1	#2	#3	#4	Direct Detection		Indirect Detection	
	Regional Appraisal	Detailed Reconn.	Detailed Surface Study	Detailed 3-D Study	Good	Questionable	High** Discrimination Capability	Low Discrimination Capability
<u>GEOLOGIC</u>								
Office compilation	X							
Photogeologic Study	X	X						
Aerial examination	X	X						
Outcrop examination	X	X	X					
Geologic mapping & investigations	X	X	X	X				
Geologic logging				X				
Boulder tracking		X	X					
<u>GEOCHEMICAL</u>								
Stream sediment sampling	X	X						
Water sampling	X	X						
Rock sampling	X	X	X					
Specialized sampling	X	X	X					
Assaying	X	X	X	X				
<u>GEOPHYSICS-AIRBORNE</u>								
Aeromagnetic surveys	X	X						
Electromagnetic	X	X						
Radiometric surveys	X							
Remote sensing surveys	X							
<u>GEOPHYSICS-GROUND</u>								
Gravity	X	X	X					
Magnetic	X	X	X					
Radiometric		X	X					
Seismic		X	X					
Resistivity		X	X					
Self-Potential		X	X					
Induced Polarization		X	X					
Down-hole electrical				X				
<u>THREE-DIMENSIONAL SAMPLING & EVALUATION</u>								
Trenching			X	X				
Rotary drilling				X				
Core drilling				X				
Tunnel/Shaft work				X				
Mineral dressing tests				X				
Economic evaluation				X				

Not a detection method
Not a detection method

* Detection refers to the ability to detect a deposit if it is there. Indirect detection refers to a geological, chemical or physical response showing a deposit may be the cause of the response; this is in opposition to direct evidence of the presence of a deposit.

** Discrimination with regard to indirect methods refers to the ability to determine if a certain response (anomaly) is due to a deposit or to another cause.

AREA, TIME AND EXPENDITURE*-----EXPLORATION FOR A PORPHYRY COPPER DEPOSIT

	Stage 1-- Regional Appraisal, One Region Selected	Stage 2-- Detailed Recon., One Target Area Selected	Stage 3-- Detailed Surface, One Target Selected	Stage 4--Detailed 3-D Physical Sampling, Target An Ore Body
Area under consideration	1,000-100,000 sq.mi.	10-100 sq. mi.	10-50 sq. mi.	3-20 sq. mi.
Cumulative expenditures	\$5,000-100,000	\$10,000-75,000	\$50,000-150,000	\$500,000-4,000,000
Cumulated elapsed time	1-12 mo.	13-18 mo.	18-24 mo.	24-60 mo.

*After Bailly, Public Land Law Conference, University of Idaho, 1966.

RATINGS OF FOREIGN COUNTRIES AS TO RELATIVE PORPHYRY COPPER EXPLORATION POSSIBILITIES

(80% Geological Favorability
 (20% Commercial Environment Favorability)

Highest

Chile (O, P, SP, G, C)

Mexico (O, P, SP, G, C)

Philippines (O, P, SP, E, E-V)

New Guinea & Islands (O, P, SP, C, E, E-V)

Alaska-Yukon (P, SP)

Peru (O, P, SP, G, C)

Iran (Query) (O, P, SP, G, C)

(USSR)

(Bulgaria)

(Query) (O, P, SP, G, C (?))

(Yugoslavia)

(Romania)

Indonesia (P, SP, G, C, E, E-V)

British Columbia (O, P, SP, C, L)

Malaysia-Kalimantan (Query) (P, SP, G, C, E, E-V)

Panama (Query) (O, P, SP, G, C, E, E-V)

Ecuador (P, SP, G, C)

Malaysia-Sabah (O, P, SP, G, C, E, E-V)

Central America (SP, C, E, E-V)

Japan (Query) (SP, C)

Greece (Query) (P, SP, C)

Columbia (Query) (SP, C, E, E-V)

Malay Peninsula (SP, G, C, E, E-V)

Caribbean (Query) (O, C, E)

Bolivia (P, SP, G, C)

Thailand (P, SP, G, C, E, E-V)

China (Query) (P, SP, C (?))

Australia (O, P, SP, C, L)

Lowest

Code O - Ore bodies, known but underdeveloped.

P - Prospects, unexplored or partially explored.

SP- Suspected Prospects---rumors.

E - Expensive, physically difficult to prospect.

E-V -Expensive, physically very difficult to prospect.

G - Either entire government control or government-owned mining companies---they get first crack at new field geological data----so, highly competitive but maybe subject to deals with foreign companies.

C - Commercial deals maybe possible, but currently laws, regulations vague or in some cases essentially prohibitive.

L - Idiotic new laws

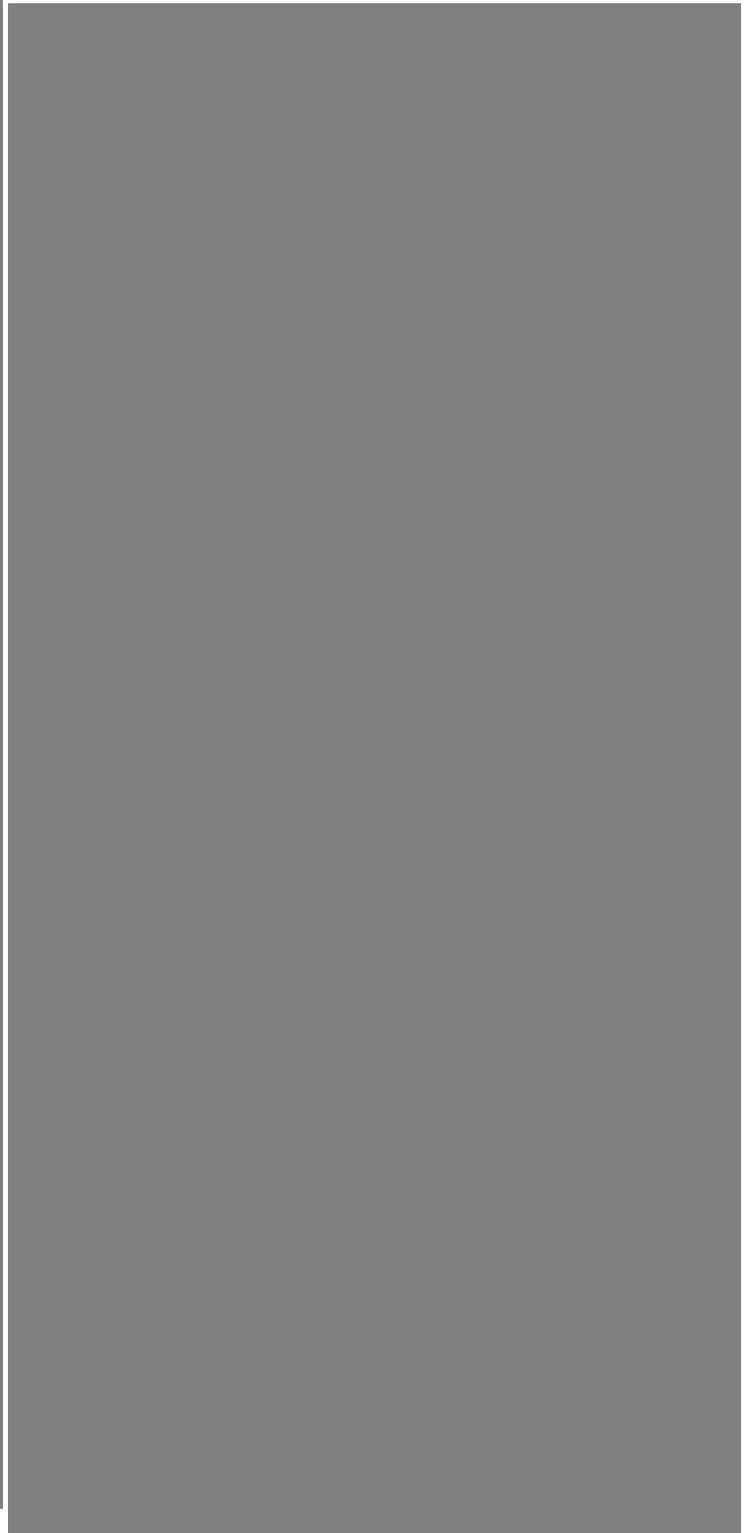
Argentina →

Note: 4/17/75 All subject to change by tomorrows' headlines. They may even be changed before the present audience gets through with me.

Kenyon Richard

◆ ◆ ◆ STRUCTURE AND MINERALIZATION
AT SILVER BELL, ARIZONA

BY KENYON RICHARD AND JAMES H. COURTRIGHT



OXIDATION, LEACHING, AND ENRICHMENT OF COPPER DEPOSITS

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*available at seminar for
reproduction

A KEY SCALE BASIS FOR CAVITY CHEMISTRY
Disseminated Copper Deposits

Showing the four main sulfides (py, cpy, bn, ccc) and all possible dual combinations calibrated to a S:Cu scale.

S:Cu awu	Sulfide aggregate vol.% in sulfide		Single sulfide & dual bleb equivalent combinations		Leaching remarks (quartz-sericite gangue)
1:0	<u>py</u> 100				Cavity cleaned of Fe and any Cu
1:0.5	<u>cpy</u> 100	<u>bn/py</u> 58/42	<u>ccc/py</u> 46/54		Cu-good leaching (c)* Fe-mostly indigenous
1:1	<u>bn/cpy</u> 70/30	<u>bn/py</u> 89/11	<u>ccc/py</u> 70/30	<u>ccc/cpy</u> 39/61	Cu-no leaching (r) Fe-all indigenous
1:1.25	<u>bn</u> 100	<u>ccc/py</u> 79/21	<u>ccc/cpy</u> 56/44		Cu-no leaching (r) Fe-indigenous
1:2	<u>ccc</u> 100				Cu-indigenous Fe-none

Symbol explanation:		Constants used in computations:		
awu	atomic weight units		Sp. Gr.	% Cu % S
bn	bornite	PYRITE	5.013	0.00 53.54
ccc	chalcocite	CHALCOPYRITE	4.283	34.64 34.94
cpy	chalcopyrite	BORNITE	5.074	63.33 25.55
py	pyrite	CHALCOCITE	5.770	79.86 20.14
c	cavity			
r	rock	ATOMIC WTS.		Cu 63.54, S 32.064

* At about 1 vol. % of total sulfides in the rock, Cu leaching would start, and it would increase with % total sulfides.

TWM, January 1973

SOME SIGNIFICANT MINERALS

Oxidation products

Hematite Fe_2O_3
 Goethite HFeO_2
 Jarosite $\text{K}(\text{FeAl})_3(\text{SO}_4)_2(\text{OH})_6$

Pitch limonite $\text{H}(\text{Fe,Cu})\text{O}_2$
 FeCuMnOx-fine grained mixture goethite, cuprite, psilomelane, etc.

Cuprite Cu_2O
 Native Cu
 Antlerite $\text{Cu}_3(\text{OH})_4\text{SO}_4$
 Brochantite $\text{Cu}_4(\text{OH})_6\text{SO}_4$

Malachite $\text{Cu}_2(\text{OH})_2\text{CO}_3$
 Azurite $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$
 Tenorite CuO

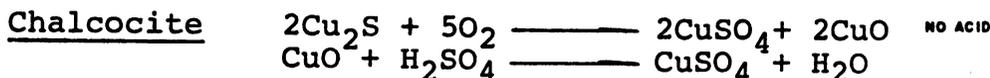
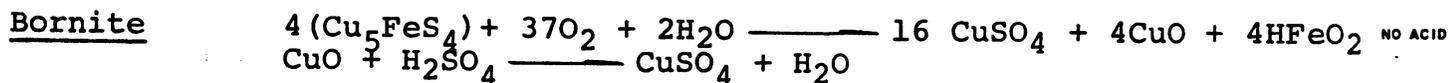
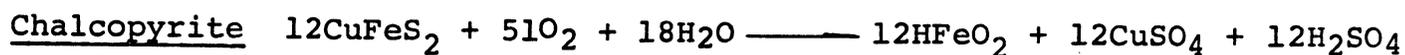
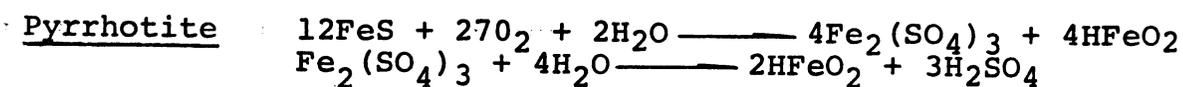
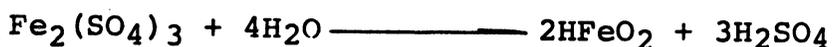
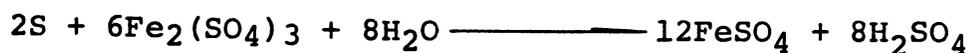
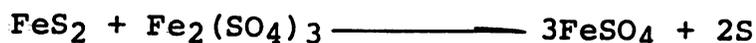
Chrysocolla $\text{CuSiO}_3 \cdot n\text{H}_2\text{O}$
 Chalcanthite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 Turquoise $\text{CuO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$
 Delafossite CuFeO_2

Ferrimolybdate $\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$
 Ilsemannite $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$
 Moly limonite $(?)\text{FeMoOx}$

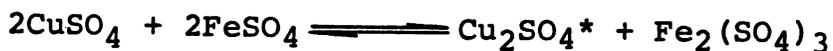
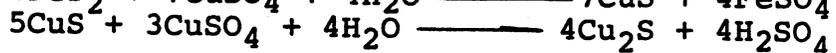
Sulfides

	<u>% S</u>	<u>% Cu</u>
Pyrite FeS_2	53.4	—
Molybdenite MoS_2	40.1	—
Pyrrhotite FeS	39.6	—
Chalcopyrite CuFeS_2	34.9	34.6
Covellite CuS	33.5	66.5
Bornite Cu_5FeS_4	25.6	63.3
Digenite $\text{Cu}_{1.88}\text{S}$	21.1	78.9
Djurleite $\text{Cu}_{1.96}\text{S}$	20.5	79.5
Chalcocite Cu_2S	20.2	79.8

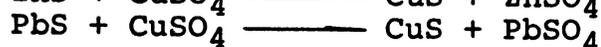
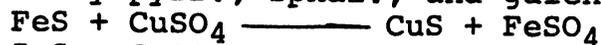
SOME INDICATED NET REACTIONS

Pyrite, oxidation of

Small amounts of cuprous sulfate (*) coexist with cupric sulfate, and the former is more active for replacement of other sulfides by Cu_2S (Zies, et al, 1916):

Replacement by chalcocite

ppt. of cv. by pyrr., sphal., and galena w/o valence change (Emmons, 1917)

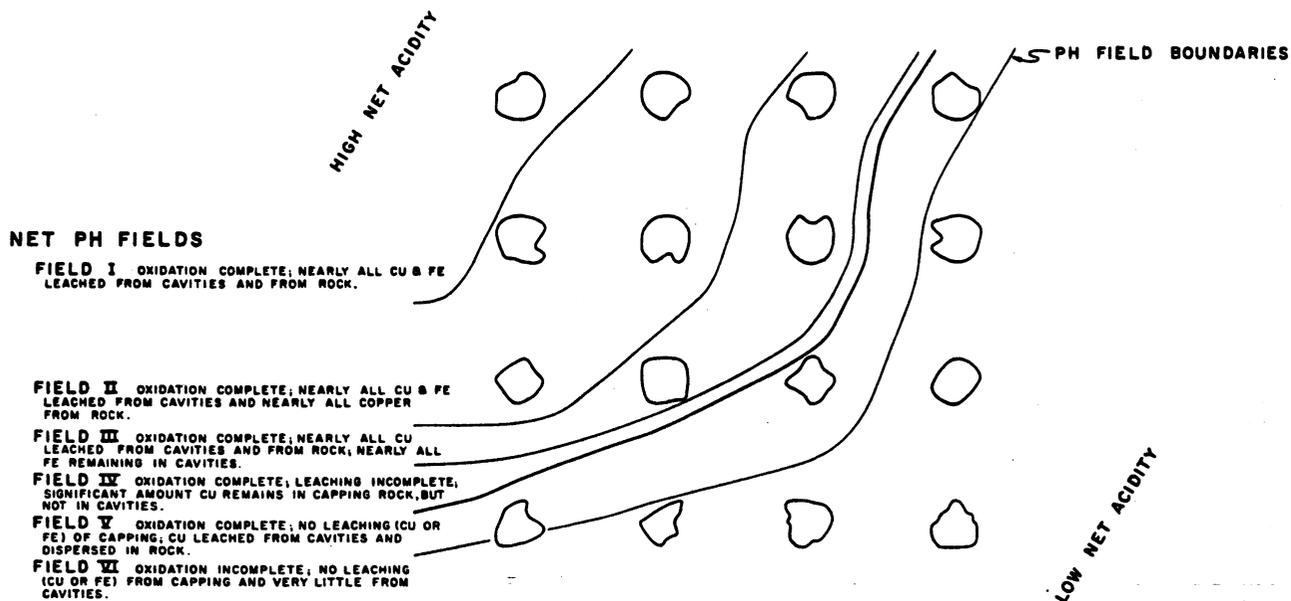
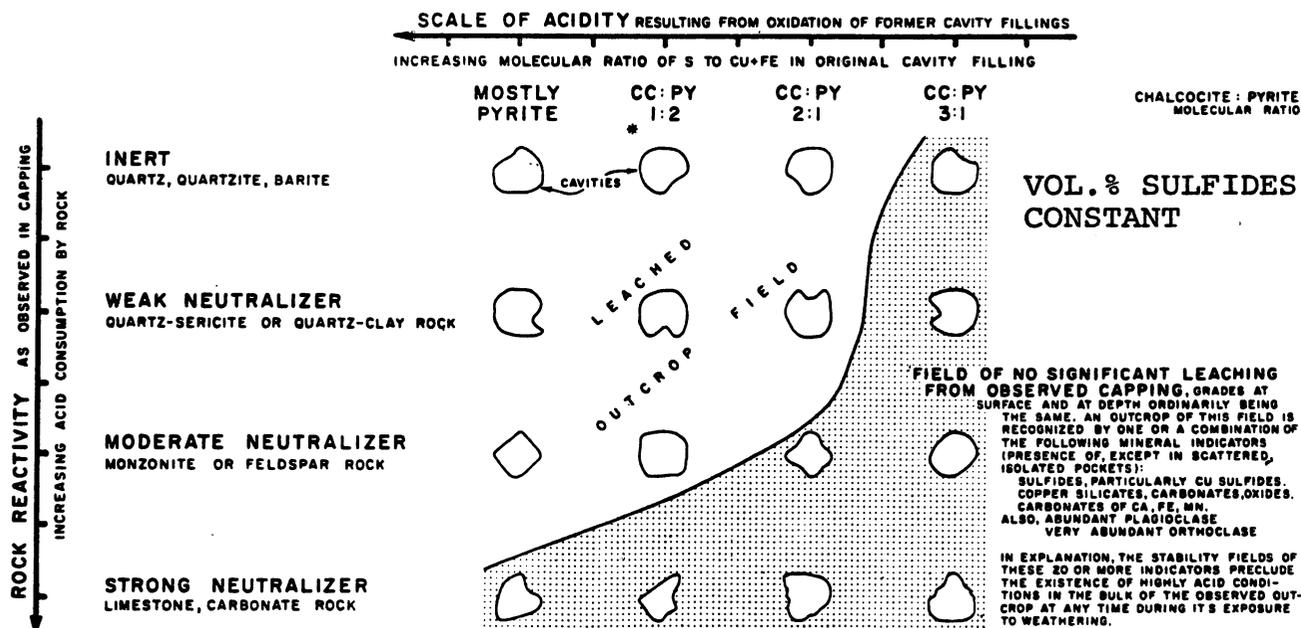


revised 3-5-74

DEPENDENCE OF LEACHING ON NET ACIDITY

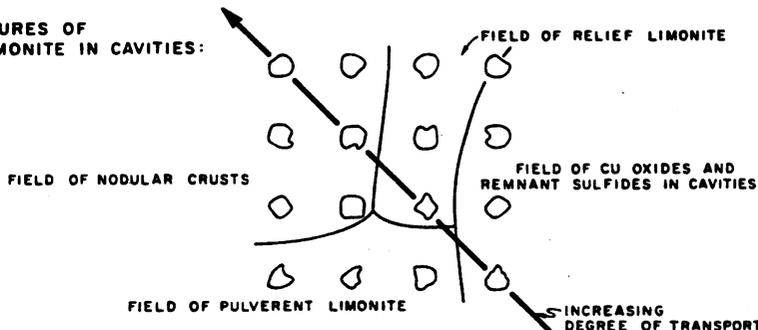
A PRIMARY ASPECT OF CLASSICAL LEACHED CAPPING INTERPRETATION[Ⓢ]

PARAMETERS: (1) LEACH WATER ENTERING AREA IS ABOUT NEUTRAL, (2) LONG EXPOSURE OF OUTCROP TO WEATHERING, (3) NO STRUCTURAL OR PRIMARY ZONAL CHANGE STRUCTURALLY BELOW OUTCROP WITHIN DRILLING RANGE.



* EQUIVALENT POSITION OF CAVITY FILLED WITH PURE CHALCOPYRITE.

TEXTURES OF LIMONITE IN CAVITIES:



Ⓢ GRAPHICALLY ABSTRACTED BY THOMAS W. MITCHAM FROM:
BLANCHARD & BOSWELL (1925) P.618,625,628,631
BLANCHARD & BOSWELL (1928) P.280-284,374-376
BLANCHARD (1939) P.352-355
LOCKE (1926) P.61,64-68,75,87-89,103-108,120-121,143
TUNELL (1930) P.13-17

A LIMONITE SCALE

(G = goethite; H = hematite; J = jarosite.)

Slow Neutralizer		Indigenous Limonites	Transported Limonites	Moderate Neutralizer	
Percent Copper ¹	Chalcocite:pyrite ratio			Chalcocite:pyrite ratio	Percent Copper ¹
	2.8:1 ²	none	none		
1.23	2.5:1	relief; fragile, fine cellular hematite	none or rare	2:1	1.16
1.16	2:1			1.5:1	1.06
1.06	1.5:1		fringing hematite	1:1	0.92
0.92	1:1	hematite relief; hard cellular		1:1.5	0.75
0.75	1:1.5	hematite relief; hard cellular; <u>rare</u> <u>botryoidal</u>	fringing; exotic hematite	1:2	0.64
0.64	1:2	hematite, <u>botryoidal</u> , hard cellular, relief; minor goethite	H>G (J?) fringing; exotic rare iridescent	1:3	0.49
0.49	1:3	hematite, botryoidal to hard compact, rare relief; minor to moderate goethite	H>G>J		
0.40	1:4	botryoidal to <u>nodular</u> ; hard compact, vitreous, flat hematite goethite	G>H>J iridescent; abundant exotic		
0.33	1:5		J>G>H		

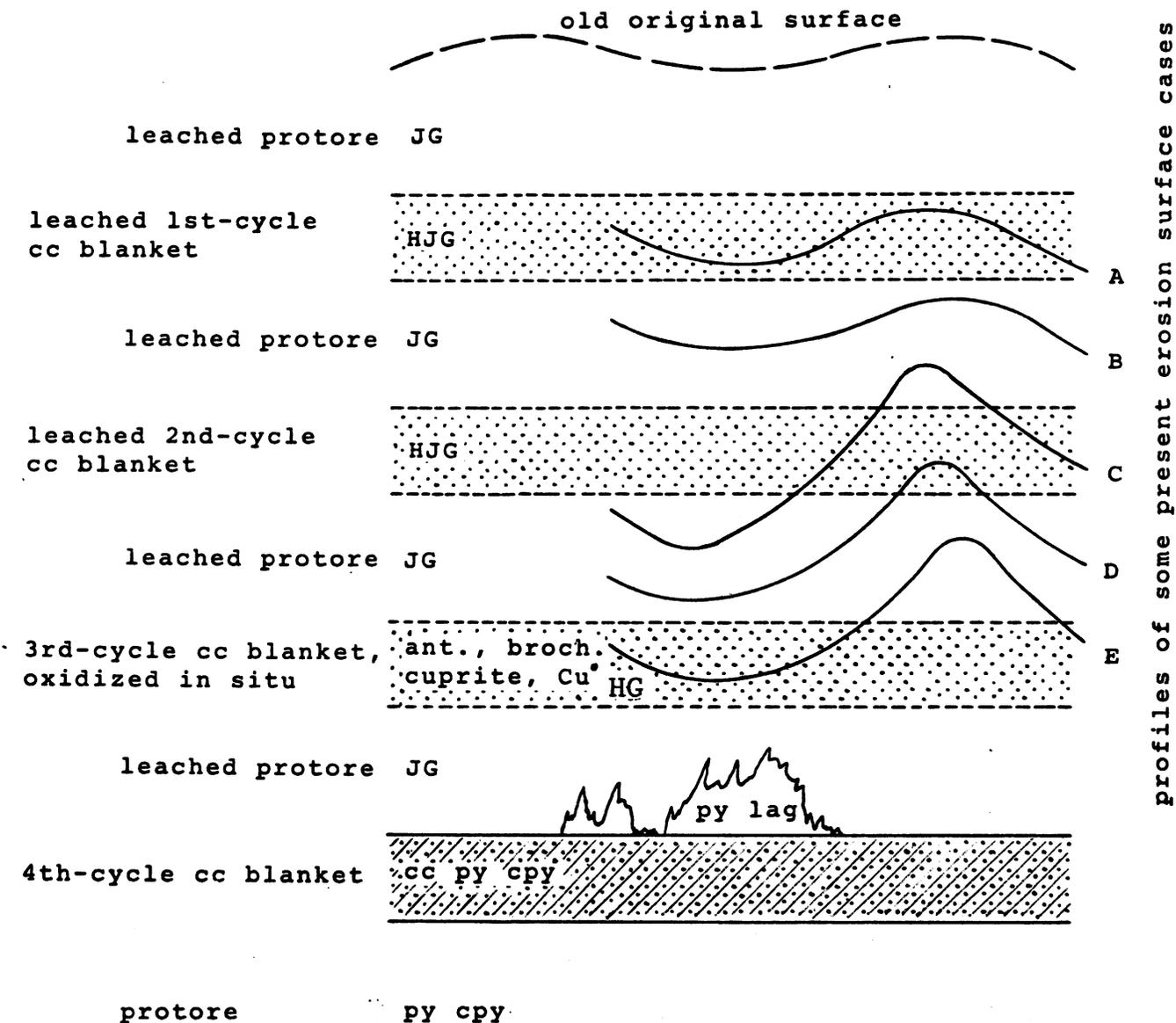
1. Percent copper per volume percent indigenous limonite cavities.

2. No leaching; copper oxides abundant; + 0.5 percent copper if sulfides exceeded 0.5 volume percent.

Modified from a draft of Loghry (1972)

4 CYCLES OF OXIDATION-LEACHING-ENRICHMENT
Section Illustrating Layering of Capping Types

Result of Water Table Lowering in Stages



Explanation

- G goethite
- H hematite
- J jarosite
- ant antlerite
- broch brochantite
- py pyrite
- cpy chalcopyrite
- cc chalcocite

OXIDATION, LEACHING, AND ENRICHMENT
OF COPPER DEPOSITS

An in-company short course offering
by
Thomas W. Mitcham

A GENERALIZED DESCRIPTION

A three-day professional improvement course on this topic is offered, involving two days of lectures and discussion and a one-day field trip. Considering the depth and scope, the treatment of field and experimental data and theory, and the resolution of these to useful applications in modern exploration, the course is believed to be truly unique.

The presentation is an in-depth attempt to explore the geologic processes involved in the chemical weathering of copper-bearing sulfide deposits, stressing the causes and effects of oxidation, leaching, and enrichment. This knowledge then is directly applied to capping interpretation, or more specifically to easily mastered, efficient techniques of quantitative prediction of sulfide mineralogy and copper grade structurally below cappings. Resolution to sulfide reconstruction is sufficiently quantitative to allow recognition of positions in reference to sulfide mineral zoning patterns in porphyry copper deposits.

The presentation is firmly rooted in the literature, but as obviously indicated by the above statements, it extends considerably beyond the literature, published or unpublished.

Although the concepts and techniques covered are applicable to copper deposits in general, the presentation is definitely slanted toward disseminated or porphyry copper deposits.

Origins of concepts & techniques.--Personal field exposure to men widely considered as among the world's best capping interpreters led the undersigned to initiate research on copper cappings about 25 years ago. Also, his investigations in recent years have benefited considerably from open exchanges with other capping investigators.

Observations on some Arizona properties 12 years ago led the undersigned to ponder on a comparison of the Blanchard (emphasis on textures) and Tunell (emphasis on supergene mineralogy) schools of capping interpretation, and he has been rather intensely involved in capping research since that time. To a

large extent, the avenues of recent investigation have evolved from a special interest in supergene minerals as indicators of sulfide mineralogy, derived from his dissertation topic, Indicator Minerals, Coeur d'Alene Silver Belt.

During the spring of 1972, while serving as visiting Professor at a Southwestern university, the undersigned prepared a series of 12 special lectures on the topic, and this led to months of additional presentation preparation.

During the week of the annual Arizona Section (AIME) meeting in December 1972, at the invitation of a major mining company, the presentation was given in Tucson to an assembled group of its staff geologists, ranging from junior men to those with over a decade of experience in copper and other non-ferrous metal exploration.

The above "test run", of course, provided an opportunity to considerably improve the presentation. In fact, additional support by the client for extended investigations resulted in very significant extrapolations and additions to the materials.

In-company short courses, general. --Occasional updated reviews on selected topics vital to a technical group's assignment is undoubtedly helpful to goal accomplishment, and the participants should include senior as well as junior men. This sounds good, but a man (or men) must be assigned to prepare the reviews.

The undersigned formerly conducted short-course and workshop programs on various topics with the able assistance of an in-house scientific group which he directed. The group was dedicated to mineral exploration research and technical improvement. However, this was the world's largest copper company, and most mining and exploration companies probably could not justify a similar program.

Open short courses on various topics related to exploration are frequently given, of course, at centers of learning and elsewhere. However, applicability gaps are usually a problem, for various reasons. One common reason is that a specialist on Technique A expands the topic to "Technique A Applied to Exploration" when the latter part of the topic is actually outside his knowledge band, resulting in a technically sound technique, per se, being carried into the realm of fantasy. Another common reason is that very little thought is given to significant justification for holding the sessions, e.g., "What's new and useful?" This often results in a hastily contrived conglomerate of rehash and speculation in a matrix of friendly conversation.

The undersigned is attempting to prepare topical presentations which will give the average mineral exploration group some of the advantages of in-company short courses. These courses, mostly in preparation, are being offered under the name of PCRG (Porphyry Copper Research Group).

The preparation level of the topic under discussion here (copper cappings) is considered as sufficient in scope and depth to justify the formal offer made herein.

Comments on attached outline.--Under the heading of Historical Review, concept development is chronologically traced from the beginning of the 20th Century, through the main era of intense capping interpretation research (1919-1930), and on through 1972.

Under Significant Minerals, compositions, physical properties, and occurrence characteristics of the various iron and copper minerals involved in or resulting from the chemical weathering of copper deposits are discussed. Twelve supergene minerals or mineraloids are flagged as indicator minerals, i.e., minerals which variously reveal chemical conditions during weathering as well as former sulfide mineralogical conditions.

With derivations from field observations, experiment, and theory, the basic Processes and their controls are explored with considerable elaboration. Supergene mineral residuals anticipated and observed after various sulfide combinations and percentages are discussed.

Ten Basic Field Observations is a check list for the field, but with elaboration on efficient techniques of recognition and recording of critical data. Data priorities are discussed, considering that some types of data are key while other types are usually desirable for confirmation only.

The concepts and techniques explored under the heading of Capping Interpretation are the core of the presentation. The broad concept stressed is that sulfide mineralogy (percent of sulfides and sulfide ratios) is reflected in the capping by supergene mineral residues--indicator minerals. Presence of the capping indicators, of course, is determined by their stability fields in reference to Eh, pH, and bulk chemistry under temperature and pressure conditions which can be assumed within narrow ranges. On a grid with coordinates of percent of former sulfides in rock and sulfide ratios, stability fields of supergene indicators are translated and platted in terms of these two reference coordinates. The indicator mineral fields, some narrow-band and some broad-band, overlap. Thus, with a set of indicator mineral readings from a given outcrop, one can enter the chart and "read-off" percent of primary sulfides, sulfide ratios, and primary grade to within useful approximations. A figure for residual copper in the capping refines the approximation. Enrichment is determined in a similar manner.

Interpretation curves, which are derived from sulfur and copper values in terms of awupm (atomic weight units per million), are a close fit to numerous field correlations.

Illustrations, general.--The presentation is graphically and liberally illustrated with tables, charts, specimens (including special limonite collections), colored slides, and blackboard sketches.

Materials issued to individual participants.--The 14 tables and charts listed in the outline are issued as individual handouts to each participant. These are specifically issued on a company-confidential basis, in consideration of the new concepts and new combinations displayed on a number of the charts, especially on charts 1, 2, 4, 5, 7, 10, 12, 13, and 14. The limonite color chart is a laminated reproduction (by Ray Manley) of what is probably the most comprehensive chart of scaled limonite mineral mixtures ever attempted. This chart is pocket size for field use. Also, a list of 40 selected references is issued to individual participants.

Materials issued to the participating company.--A set of reproductions of 17 key articles, selected from the list of 40 references, are issued to the participating company. These are either in report covers or soft-covered Xerox reproductions from University Microfilms. In addition, one complete set of materials issued to individual participants is also issued to the company involved.

Arrangements and terms.--The program, material issues, and arrangements are planned to accomplish the prime objective of the offering. This is to "reach" every individual participant with an in-depth professional experience, meaningful and useful to him and thus to his company. Because demonstrations, working with specimens, and discussions are involved, the objective is best accomplished in a small group.

At least for the present, the undersigned is definitely not inclined to "go public" with this short course, i. e., to offer it on an individual fee basis. The presentation is offered only on an exclusive in-company basis, so that the topic can be fully treated, including the full and open discussion of the latest observations, derivations, and concepts. The offering is made only to mining companies and valid mineral exploration companies. It is not made to other types of professional groups or to individual geologists, per se.

Individual participants must be full-time employees of the subscribing company. Also, the participating company is specifically requested to clearly advise its participants prior to the sessions that the course content details (especially issued materials) be treated as company-confidential. This is not intended to restrict later dispersion of the contents or reproduction of materials within the participating company providing it is done on a company-confidential basis. These company-confidential treatments are simply requested in good faith, with no intention whatever to hold the company involved responsible for the extent to which its employees abide by company directives.

The two days of presentation and discussion can be given about anywhere, but considering the desirability of a field trip on the third day, the session is best held at a location near a porphyry copper deposit with some weathered outcrops. Meeting room arrangements can be made by the participating company or PCRG will make them and bill the company for direct cost.

Selection of one of the company's deposits with remnant cappings is suggested for the field trip. In cases where this is not possible, the undersigned can suggest a mine with good remnants of weathered cappings to be visited, but arrangement with the mine management is best handled by the participating company.

The base professional fee for the short course is \$3,000, regardless of the number of participants. This fee covers all issued materials and travel time (if any) up to a total of two days. Travel time in excess of this would be billed at the rate of \$200/day. Travel expense (if any) is billed at cost.

The maximum number of participants recommended is 10, but a total of up to 15 will be accepted.

If, by their mutual arrangement, 2 or 3 companies wish to participate in the same session under the single base fee, this will be considered, except that a single \$100 extra charge for company-issued materials will be applied for each additional company.

In the case of joint sessions, other arrangement understandings discussed above, e.g., company-confidential treatment and full-time employees only, would apply to each company participating.

Applicability of concepts and techniques. --Although the advantages of capping interpretation are obvious to copper exploration men, a few comments apropos to the modern exploration scene will be attempted at this point.

In heavily explored areas as the western United States, untested large "red thumbs" where the canyon walls are peppered with "live limonite" probably no longer exist. Occurrences such as this represent a special case, multicycle enrichment where a destroyed chalcocite blanket is exposed. Capping interpretation in the Western States today must be much more sophisticated than simply recognizing this special case.

We should be able to effectively handle cappings where little or no enrichment is involved, i.e., to "read" primary grade and primary sulfide mineralogy from thoroughly oxidized or leached cappings, both over ore and over sulfide zones near ore. Further, we should be able to recognize single-cycle enrichment, and depending on exposures, to anticipate the number of cycles of enrichment. Available weathered exposures are often not only small and limited, but they are not likely to be structurally over the ore shell of the sulfide zoning pattern. The exposures may be "peek" rock bit holes through cover, small windows of bedrock, or small exposures at the edge of cover.

In summary. --The level of copper capping interpretation presented is considered to be sufficiently advanced in sophistication to handle many of the special capping problems faced today in heavily explored areas and to handle

"classical" cappings more effectively. Considering depth, scope, and resolution to usefulness, the presentation may be the most comprehensive treatment of copper cappings ever attempted.



Thomas W. Mitcham

February 12, 1973
Revised: February 12, 1975

Attachments:
Course outline (2 pages)

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TULSA, OKLAHOMA 74104

OXIDATION, LEACHING, AND ENRICHMENT
OF COPPER DEPOSITS

Short Course Outline

INTRODUCTION

HISTORICAL REVIEW

1900-1972 The men, their contributions, breakthroughs

SIGNIFICANT MINERALS

Supergene Fe indicator minerals (3)
Supergene Cu indicator minerals (7)
Supergene Fe-Cu indicator "mineraloids" (2)
Other oxidation products of Cu-Fe sulfides
Some discredited supergene minerals (5)
Sulfide minerals

PROCESSES

Oxidation
Leaching
Enrichment
Multicycle enrichment
Blanket positions, laterally
Age of enrichment
Climate & topography
Cavity chemistry

TEN BASIC FIELD OBSERVATIONS

Sulfide minerals, if any
Supergene Cu minerals
Supergene "mineraloids"
Supergene Fe minerals
Texture & distribution of "limonite"
Volume % of cavities
Residual Cu content of capping
Reactivity of gangue
Capping classification
Structural features

CAPPING INTERPRETATION, QUANTITATIVE

Primary grade & primary sulfide mineralogy
Enrichment, single cycle and multicycle

(Continued, next page)

Short course outline, continued

REFERENCES (40), individual issue

TABLES & CHARTS (14), individual issue

1. Key scale basis for cavity chemistry
2. Some significant minerals
3. Indicated net reactions
4. Stability field experiments
5. Leaching & net acidity
6. Volume % chart
7. Texture-distribution scale
8. Limonite scale
9. Morenci system
10. Primary sulfides & grade correlated with supergene mineralogy
11. Savanna climate
12. Enrichment cycles
13. Porphyry copper zoning & capping types
14. Limonite color chart, prepared from 20 controlled mixtures of goethite, jarosite, and hematite