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AN EARLY POTASSIC TYPE OF WALL-ROCK ALTERATION AT BUTTE, MONTANA

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ABSTRACT

Deep mine levels at Butte, Montana, have recently exposed narrow but well-defined envelopes of wall-rock alteration adjacent to molybdenite-bearing quartz veinlets. Within the envelopes the feldspars and micas are altered to a fine-grained assemblage of muscovite, biotite, alkali-feldspar (Or_{70}), and quartz, together with anhydrite, carbonate, magnetite, hematite, pyrite, and chalcopyrite. The quartz-molybdenite veinlet itself may also contain small amounts of any of the foregoing minerals except biotite. At their outer edges the alteration envelopes grade into fresh quartz monzonite. There is no marginal argillic zone.

These veinlets and alteration envelopes are cut and offset by white quartz veinlets which contain no molybdenite and have no alteration envelopes around them. And *both* types of veinlets are cut and offset by still later fractures of all sizes, which control the concentric sericitic and clay mineral alteration envelopes of the "main-stage" pyrite-rich copper and zinc veins.

INTRODUCTION

Professor Kerr is one of the foremost students of hydrothermal wall-rock alteration and has long shown friendly and helpful interest in Anaconda's study of the ore deposit at Butte, Montana. So it is a pleasure to contribute in his honor this brief description of a type of wall-rock alteration which has been exposed by deep mine workings at Butte in recent years.

DISTRIBUTION AND STRUCTURAL RELATIONS

The deepest mine workings in the Butte District are near the geographical center of the District, west of the "Central Zone" of pervasive sericitization and pyrite-chalcocite ores (Sales, 1913). Here mining has penetrated to depths of about 5000 feet on the great chalcopyrite orebodies of a number of large "Anaconda" and "Blue" veins. These large veins are encased in normal "main-stage" sericitic and argillic alteration envelopes similar to those described in an earlier paper (Sales and Meyer, 1948). The large veins are far enough apart, however, that envelopes of argillic alteration from adjacent veins do not overlap, and unargillized Butte quartz-monzonite is preserved between them. In this otherwise fresh quartz monzonite, dark gray alteration envelopes have recently been observed along quartz-molybdenite veinlets. Most of the veinlets are less than 1 inch thick, discontinuous along strike, and variable in dip. The envelopes range in thickness up to about 8 inches, with the veinlet at the center. There is no megascopically visible zoning in the alteration envelopes between veinlet and fresh rock except a slight darkening of the color at the outer fringe of the envelope owing to an increase in proportion of biotite relative to muscovite.

The veinlets and their alteration envelopes are cut and offset by similar veinlets of white quartz which contain *no* molybdenite and show *no* alteration against fresh quartz monzonite. Such white quartz veinlets are common elsewhere in the district. Like the quartz-molybdenite veinlets, they fill simple cracks, show little or no evidence for replacement of the wall-rock, and frequently appear to fill in between jagged dilated walls. They are also discontinuous in strike and variable in dip, and they rarely exceed about 2 inches in thickness.

Both types of quartz veinlets are cut and offset by any vein or veinlet which carries "main-stage" copper, zinc or manganese mineralization and is bordered by concentric sericitic and argillic alteration envelopes. Thus there is indisputable structural evidence that the quartz-molybdenite veinlets and their dark-colored alteration envelopes were formed in the deep levels of the district before the beginning of the faults which subsequently guided the main hydrothermal inundation.

Mineral Assemblages

The early dark micaceous (abbreviated EDM) alteration is characterized by potassium fixation in biotite, muscovite and alkali-feldspar. Chlorite, anhydrite, calcium-bearing sidero-magnesite, magnetite, hematite, pyrite and chalcopyrite are also quantitatively important, and fluorite and molybdenite are present locally in small grains.

Biotite. Fine-grained (*ca.* 0.01–0.10 mm.) light-brown and light-green biotites are conspicuous in thin section and give the dark olive-gray color to the hand specimen. They replace hornblende, darker brown Ti-rich biotite, oligoclase-andesine and, near the veinlets, even K-feldspar in the original quartz monzonite. They are intimately mixed with colorless mica, particularly where they replace the feldspars.

Both the brown and the green biotites are low in TiO_2, but they have only slightly higher Mg/Fe ratios than the biotite in the original rock. Both are fully trioctahedral and show no 14 or 7 Å spacings. Possibly the green color is consequent from an increase in Fe^{2+}/Fe^{3+} ratio, but it is not clear at present how the charge difference is compensated. Infrequently, color transition from green to brown can be seen in a single grain of alteration biotite, but usually domains of green a millimeter or more in diameter are dispersed in brown. If both plagioclase and K-feldspar are biotitized, there is more green in the K-feldspar and more brown in the plagioclase. The green biotite also tends to concentrate at the contacts between an altering biotite plate and adjoining feldspars, the center of the biotite plate altering to a mosaic of tan Ti-free biotite.

Muscovite and Alkali-Feldspar. Muscovite (mostly 2M polytype) is the dominant phase replacing the feldspars. Plagioclase is attacked farther from the veinlet than K-feldspar, and the muscovite which replaces it commonly shows little or no preferred orientation along the plagioclase cleavage. Biotite, quartz and untwinned alkali-feldspar (Or_{70}) are all present with the muscovite.

Muscovite replacing the K-feldspar of the original rock shows a very unusual textural relationship to associated quartz and new alkali feldspar. The muscovite is separated from the quartz by uniform thin rims of new untwinned alkali-feldspar which *look* like reaction rims between the muscovite and the quartz. Either the muscovite and the feldspar grew together at equilibrium, with the feldspar tending to be stabilized by higher activity of silica adjacent to the quartz grain, or the reaction to feldspar was accomplished after initial crystallization of a muscovite-quartz assemblage, probably because of an increase of temperature or activity of potassium. Such rims of alkali-feldspar are found at Butte only in the early dark micaceous alteration assemblage—never in the alteration zones of the main hydrothermal stage. There is no evidence for change in volume during the reaction.

Sulfates, carbonates, oxides and sulfides. Anhydrite is a very important wall-rock alteration product as well as vein constituent in the EDM environment. It is present in contact with all other mineral phases of the alteration assemblage. Locally it is abundant in replaced plagioclase and biotite(?) grains, poikilitically enclosing micas and other alteration minerals. The EDM environment is the only place where anhydrite is found in the Butte District. It is also interesting to note that where EDM veinlets and alteration envelopes are exposed to later main-stage hydrothermal mineralization and alteration at Butte, the anhydrite is usually removed, leaving cavities and vugs. Anhydrite is apparently a soluble phase during main-stage hydrothermal activity.

Carbonate is also present in the EDM envelopes and veinlets. Usually it is present in volumes once occupied by hornblende or plagioclase, but it may also be found as isolate grains in the replacement mosaic of any other wall-rock constituent. As mentioned earlier, it is sidero-magnesite, with a Ca/Mg+Fe ratio about 1 to 4.

Magnetite is present in nearly all samples of the EDM alteration envelopes, and locally is an abundant constituent in the quartz veinlets which are central to the envelopes. Usually there is a bit of oxidation to hematite in grid patterns or along the margins of grains.

In addition to molybdenite, pyrite and chalcopyrite are the only sulfides found in the EDM environment. Both are more abundant in the alteration envelopes than in the veinlets, and they seem to be clustered in places once occupied by the mafic minerals of the original quartz-monzonite. By significant contrast, in main-stage mineralization, virtually all of the copper is in the veins and veinlets, and the only abundant sulfide in the wall-rocks is pyrite.

Chemical gains and losses. Between the well-defined envelopes of early dark micaceous alteration, the Butte quartz-monzonite shows less hornblende and andesine, more K-feldspar and biotite and sometimes also more quartz than is normal in other parts of the district. It is also studded with dispersed grains and tiny veinlets of sulfide—chiefly pyrite but also some chalcopyrite. The distribution patterns of these variations are not yet sufficiently well known to review systematically, but they necessitate caution in evaluating the chemical gains and losses in the EDM envelopes with respect to the immediate rock around them. Is this rock itself an alteration product by action of epigenetic solutions from a deeper source, or are we nearing a "collecting zone" or "sub-hood cupola" as postulated by Reno Sales in his Jackling Lecture of 1954?

The EDM envelopes have only a slightly higher specific gravity (2.78) than the surrounding rock (2.70) owing to the abundance of biotite and muscovite and the small amount of disseminated sulfide. Taking this into account (assuming no volume change) the constancy of alumina at about 350 mg./cm^3 prevails in the EDM alteration just as it does in the argillic and sericitic zones of the subsequent "main-stage" alteration. Magnesia is also in near-balance in the EDM envelopes with respect to surrounding quartz monzonite, but a small amount of silica and $\frac{1}{2}$ to $\frac{2}{3}$ of the CaO and Na_2O are lost. K_2O shows a gain of more than 50%, total Fe a gain of about 10%, and, of course, H_2O, S, CO_2 and SO_4 are all substantially higher in the altered envelopes.

In balance, there appears to be slight base-extraction from the EDM envelopes, evidently by hydrolytic reactions between the original wall-rock minerals and solutions which permeated along the veinlets. But this base-extraction is much more selective and far less profound than the base-leaching which accompanied main-stage mineralization along the later large veins of the district. The "main-stage" solutions removed nearly all the lime and soda and $\frac{2}{3}$ of the magnesium from the wall rocks in the alteration zones close to the veins, and added no potassium. Also silica was heavily extracted from the argillic envelope and only slightly added to the sericitic envelope. Much sulfur was added to form pyrite from all the iron in the sericitic envelope, but nearly all the copper remained in the veins. The only insoluble sulfate in "main-stage" mineralization and alteration is barite, and this is in very small amounts. Carbonate is present in main-stage alteration only in the outer argillic zone even adjacent to rhodochrosite veins, and here it is calcite rather than sidero-magnesite.

Evaluation of mineral assemblages. The most significant mineralogical difference between EDM and "main-stage" alteration at Butte is the fact that the plagioclase of the quartz-monzonite is immediately converted to the potassic minerals muscovite (Kerr, 1951), biotite and K-rich feldspar, plus quartz, rather than progressively leached to montmorillonite and kaolinite. Excluding the biotite-sulfide equilibrium momentarily, three parameters are most significant to equilibria among the feldspars, micas and clays; activity ratios of $K^+/Na^+/H^+$ (Hemley and Jones, 1964), activity of silica, and temperature. At equivalent activities of silica, higher temperature and/or higher ${}^aK^+/{}^aH^+$ would favor the EDM assemblage over the argillic assemblage (Hemley, 1959). The crystallization of quartz with the muscovite in EDM alteration suggests that the activity of silica in that system was maintained in equilibrium with quartz, whereas in the argillic alteration at Butte there is neither precipitation of quartz nor dissolution of quartz, even though silica is extensively removed from the argillic zone by argillization of the plagioclase. In the argillic zone, then, the solubility of silica may have soared metastably far above its equilibrium value, with consequent tendency to preserve K-spar in metastable association with kaolinite (Fournier, 1964).

The partitioning of iron between green and brown biotite (where it is probably in two oxidation states), magnetite-hematite, carbonate, and the various sulfides is difficult to treat except in a very general way. Assuming an aqueous system, the EDM assemblage certainly suggests lower sulfide ion activity than does the pyrite-bornite-chalcocite-sericite assemblage of Butte's Central Zone. The presence of anhydrite in the EDM alteration and its removal by "main-stage" solutions is consistent with this estimate. But before it is concluded that EDM and "main-stage" solutions were essentially different in bulk chemical composition, it must be remembered that the equilibria in question are unquestionably temperature dependent. The complex biotite-rich assemblage, with intermediate sulfide ion activity, is favored by higher temperature, though this relationship is difficult to quantify at present.

As we have seen, the gross alteration effect of both EDM and "main-stage" solutions is to leach base from the wall-rocks, substituting hydrogen ions hydrolytically. Of course, the fact that the amount of base in a given increment of solution is rising does not necessarily mean that the pH of that solution is also rising, since the pH will depend on the *relative rates* of generation of H^+ by dissociation and the loss to the wall-rocks by reaction. If the hydrogen ions are furnished continuously through increased dissociation in the solution owing to cooling, then the EDM and "main-stage" solutions could merely be at different stages in their evolution during the cooling process. If this were true, a geologic model is required which permits the "cooler" effects to be superimposed, in later structures, on the "hotter." A classical gradually retreating "source zone" is an obvious suggestion, with hydrothermal fluids evolved by crystallization differentiation over a long period of time—long enough for the batholith to have cooled through at least 100° C. at the point of reference. Of course, the foregoing model presumes a sufficiently high pressure to maintain a dense gas or liquid fluid.

Evidently geochemical evolution of the granodiorite-copper system at Butte missed none of the essential steps of the porphyries (see Meyer and Hemley, 1959), but the effects are spread out over a greater vertical distance owing to the different structural history during crystallization of the parent magma.

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REFERENCES

FOURNIER, R. O. (1964) Unpublished manuscript.

HEMLEY, J. J. (1959) Some mineralogical equilibria in the system K_2O-Al_2O_3-SiO_2-H_2O. *Am. Jour. Sci.* **257,** 241–270.

——— AND W. R. JONES (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. *Econ. Geol.* **59,** 736–569.

KERR, P. F. (1951) Alteration features at Silver Bell, Arizona. *Geol. Soc. Am. Bull.* **62,** 451–480

MEYER, C. AND J. J. HEMLEY (1959) Hydrothermal alteration in some granodiorites. *Natl. Conf. Clay Minerals, 6th, Berkeley* 1957, *Proc.*, 89–100.

SALES, R. H. (1914) Ore deposits at Butte, Montana. *Am. Inst. Min. Met. Engrs. Trans.* **46,** 3–106.

——— (1954) Genetic relations between granites, prophyries and associated copper deposits. *Am. Inst. Min. and Met. Engrs. Trans.* **199,** 499–505.

——— AND C. MEYER (1948) Wall-rock alteration at Butte, Montana. *Am. Inst. Min. and Met. Engrs. Trans.* **178,** 9–35.