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Hydrothermal Alteration at Endako — A Comparison to Experimental Studies

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ABSTRACT

The significance of K-feldspar-bearing and sericite-bearing envelopes within the pervasively kaolinized rocks of the Endako molybdenite deposit may be explained in the light of experimental studies by J. J. Hemley of the system K_2O — Al_2O_3 — SiO_2 — H_2O.

The relative vein sequence of hydrothermal alteration products is illustrated more distinctly at Endako Mines than in many of the porphyry copper deposits. Cross-cutting relations indicate a relative age sequence among the various silicate stages which is in agreement with a chemical control based on the activity ratio of K^+/H^+ in a nearly isothermal environment.

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INTRODUCTION

THIS PAPER IS PRESENTED to illustrate that the products of hydrothermal alteration and their interdependence can be readily explained in terms of the experimental work of J. J. Hemley in the system K_2O - Al_2O_3 - SiO_2 - H_2O. Many of the porphyry copper type of deposits (excluding Butte) do not show the relative alteration sequence as distinctly as it is seen at the Endako molybdenite deposit (Titley and Hicks, 1966).

Endako Mines is located 100 miles west of Prince George and about 350 miles north of Vancouver at the geographical center of British Columbia. The molybdenum deposit occurs in the Endako quartz monzonite, which is one of the oldest rock types of the composite Topley Intrusive and which has been dated at 140 m.y. (White *et al.*, 1967). The batholith is considered to be of Jurassic age (Armstrong, 1949, p. 92). The regional geology and structural interpretation of the Endako deposit was presented at the 1966 CIM B.C. Section convention in Victoria (Kimura and Drummond, 1966). The area was also covered by the B.C. Department of Mines (Carr, 1965).

The Endako orebody is an elongated elliptically-shaped stockwork which strikes N70°W, dips 20 to 50 degrees south, and measures about 6,000 feet long by 1,200 feet wide. Ore reserves as of March 15, 1968, at a 0.08 per cent MoS_2 cutoff, were 239,000,000 tons grading 0.15 per cent MoS_2. The mill capacity has been expanded to 22,000 tons per day. The average strip ratio for the ore reserves within the current ultimate pit outline is 0.5:1.

MINE GEOLOGY

The Endako quartz monzonite and three mineralogically distinct pre-mineral dykes form the host for the mineralized stockwork. The Endako quartz monzonite is generally equigranular (3-4 mm), with some K-feldspar crystals occasionally as large as 7 mm. This size difference imparts a suggestion of a porphyritic texture, but is not sufficiently distinctive to warrant the term "porphyritic." The rock is composed of quartz (30%), pale pink to orange-tinged K-feldspar (perthitic orthoclase, $2V_x$ large) (35%), white to greenish-tinged plagioclase (An_{20}) (30%) and partly chloritized black biotite (5%). Apatite, zircon, pyrite and magnetite comprise the accessory minerals. The K-feldspar/total feldspar ratio may vary between ⅔ and ½, but is predominantly ½. Therefore, the rock type is classified as quartz monzonite rather than granite.

Aplite is the least abundant dyke rock in the mine. It is typically fine-grained, pink, graphic-textured and composed of quartz (40%), pink orthoclase (40%), white plagioclase (An_{20}) (20%) and less than 1 per cent chloritized biotite.

Porphyritic granite is more abundant and has large Carlsbad-twinned orthoclase phenocrysts (1 cm) (3%) scattered through a finer grained, phaneritic, seriate-textured matrix (0.1-1 cm). The seriate matrix is composed of quartz (20%), K-feldspar (45%), plagioclase (25%) and biotite (5%). Zircon and apatite comprise the accessory minerals. Porphyritic granite dykes have only been observed to intrude the Endako quartz monzonite in the mine area and are, in turn, intruded by quartz-feldspar porphyry.

Quartz-feldspar porphyry is the most abundant dyke rock in the mine vicinity. Two phases have been observed: (1) a brown to pink rock composed of K-feldspar (orthoclase, $2V_x$ large) (2 mm) (1-5%) and (2) a brown rock with quartz (5-10%), K-feldspar (1-5%) and sagenitic biotite (1-3%) phenocrysts (1-2 mm) in a dense, aphanitic matrix (0.05 mm). The latter is termed the quartz-feldspar porphyry-biotite phase and, characteristically, contains scattered K-feldspar phenocrysts which may be up to 1 cm in length. The matrix is composed of quartz (50%), K-feldspar (40%), plagioclase (5%), biotite (5%), and accessory amounts of apatite and zircon. Quartz-feldspar porphyry intrudes the Endako quartz monzonite, aplite and porphyritic granite, which indicates that this dyke is the latest pre-ore dyke in the mine area.

Post-ore basalt dykes cross-cut the quartz monzonite, the pre-ore dykes and the mineralization.

MINERALOGY, ALTERATION AND RELATIVE VEIN AGE

Detailed megascopic, petrographic and X-ray diffractometer studies have been conducted on the vein mineralogy and on the attendant hydrothermal alteration. Comparisons of vein and specific types of alteration allow the formulation of a mineralization sequence.

A. Alteration Mineralogy

The presence or absence of specific mineral phases and their relationship to each other is the essence of an alteration study. It is essential that introduced or secondary features are not mistaken for primary variations within the Endako quartz monzonite hoist.

X-ray analysis of the fine-grained alteration clay minerals without the use of D.T.A. (Differential Thermal Analysis) or heat treatment facilities will allow only an approximate identification. Consequently, the terms sericite, kaolinite and montmorillonite refer, respectively, to the presence of a 10Å mica group mineral, a 7Å kaolinite group mineral and a 14Å montmorillonite-type mineral. Where present, the latter are glycolated and the shift in 14Å peak is checked. Polymorphs of sericite as outlined by Velde (1965) were not determined.

Three distinct hydrothermal alteration phases are observed within the Endako ore zone: (1) envelopes with K-feldspar; (2) envelopes with sericite; and (3) pervasive kaolinization. An envelope is defined as a band or zone of introduced silicates around a central vein or fracture. Pervasive alteration of the quartz monzonite is always present to some degree on the outward side of the envelope.

1. K-feldspar-Bearing Envelopes

Evidence of hydrothermal K-feldspar is seen in three distinct megascopic forms. Envelopes from ⅛ to 2 inches in width, which may be developed adjacent to either quartz or quartz-molybdenite veins, are composed of either K-feldspar (100%) or K-feldspar (95%) and quartz (5%). No other silicates or metallic phases are present in the envelope.

A second type of envelope is composed of K-feldspar (90%) and biotite (10%) in which quartz may locally be present in amounts of up to 5 per cent. The K-feldspar-biotite assemblage may also form lenses without the presence of a central vein. These lenses appear to have been developed along fractures and veins in widths of up to 24 inches. Envelopes are much more common than the lenses.

A third type of envelope is distinctly different in that it contains K-feldspar (60% or more), quartz (30%), biotite (up to 5%) and altered plagioclase (5% or more). This type appears to involve a relative increase in K-feldspar/total feldspar ratio over that which occurs in the adjacent pervasively altered quartz monzonite (quartz (30%), K-feldspar (35%), plagioclase (30%) and biotite (5%)).

The use of field or textural evidence appears to be the only reliable method to distinguish hydrothermal K-feldspar (envelopes) and primary K-feldspar (original constituent of quartz monzonite). Petrographic work shows that the hydrothermal K-feldspar has replaced the constituents of the original rock adjacent to the vein.

The degree of triclinicity of primary and secondary K-feldspar was compared using an X-ray diffractometer. Two modifications of K-feldspar are orthoclase (monoclinic, disordered) and microcline (triclinic, ordered). With falling temperature, disordered orthoclase will become more ordered and its structure will become progressively triclinic. X-ray analysis showed that only the disordered, monoclinic form of orthoclase is present in the samples examined.

Observations indicate that pink or salmon-coloured K-feldspar can exist either in envelopes or as a primary constituent. It is also possible to get both colours in the K-feldspar crystals without any apparent optical difference in thin section. Under high magnification, the salmon pink portion may show the presence of minute red specks which could be finely divided powdery hematite.

2. Sericite-Bearing Envelopes

A grey, megascopically sharp envelope borders on quartz-molybdenite and/or magnetite and on quartz-pyrite veins in widths of from ⅛ to 2 inches. This type of envelope is composed of quartz (55 to 60%), sericite (10Å) (30 - 35%) and finely disseminated pyrite (1 - 5%). X-ray diffractometer patterns of the envelopes show an absence of kaolinite (7Å) or montmorillonite (14Å) peaks. Within the envelope, the original K-feldspar, plagioclase and biotite in the rock have been replaced by sericite and quartz. Iron from the breakdown of the biotite has been sulphidized to form pyrite. Sericitic envelopes are less common than K-feldspar-bearing envelopes.

In only a few cases, the development of the envelope does not appear to be complete. In these, sericitized biotite, relict feldspar and a fine-grained currently unidentified mineral may be present in addition to the quartz, sericite and pyrite. The unidentified mineral is white or grey and has the following properties in thin section: colourless, untwinned, low negative relief with respect to Canada balsam, birefringence of about .007, optically positive (?) with $2V_z$ large (?), and with 'r' less than 'v' about Z. These properties agree with gypsum, but the presence of gypsum has not been confirmed.

To date, three examples of quartz-sericite-pyrite envelopes have been observed adjacent to a vein in which a pink mineral occurs in addition to the regular vein phases. Peterson, Gilbert and Quick (1946), who worked on the Castle Dome deposit in Arizona, described quartz-sericite-pyrite envelopes in which the original orthoclase is unstable and is altered to sericite while, at the same time, adularia (disordered, low-temperature modification of orthoclase) is deposited in the vein. Their description could also supply to those few cases of a pink mineral in a vein with a sericitic envelope at Endako. The significance of this assemblage is difficult to assess because of their limited occurrence.

3. Pervasive Kaolinization

Plagioclase is the most sensitive indicator of progressive pervasive alteration which occurs between the outer limit of an envelope and fresh quartz monzonite. The mineralogical change from hard grey plagioclase in fresh rock to a soft greenish mixture of kaolinite and sericite is sufficiently distinct to allow classification.

(a) Unaltered Quartz Monzonite — Fresh equigranular quartz monzonite is composed of quartz (30%), pink K-feldspar (perthitic orthoclase, $2V_x$ large) (35%), hard grey plagioclase (twinned and generally not zoned, $2\theta(131) - 2\theta(1\bar{3}1) = 1.50$ (AN_{20}) (30%)) and black biotite (5%). Accessory minerals are apatite, zircon, sphene and magnetite.

(b) Weak Kaolinization — Weakly kaolinized quartz monzonite contains quartz (30%), pink orthoclase (35%), greenish grey plagioclase (30%) and black or chloritized biotite (5%). Accessory minerals are apatite, zircon and magnetite or powdery hematite. The greenish-tinged plagioclase generally shows a hard grey rim and a softer greenish core. X-ray analysis of the core and rim indicate that the plagioclase is An_{20} ($2\theta(131) - 2\theta(1\bar{3}1) = 1.50$) and that the major alteration products are kaolinite and sericite. Minor amounts of a montmorillonite-type clay are locally present where the soft core has white 'specks' which will noticeably swell when a freshly broken rock surface is exposed to the air. Montmorillonite-type clay occurs only in the weakly kaolinized rock.

In thin section, minute amounts of a carbonate are seen along with a brownish to greenish, weakly pleochroic mineral which may possibly be a mixture of the clay minerals and chloritized biotite or chlorite. This greenish mineral is generally confined to certain more calcic zones which existed in the original plagioclase. It may also be found along minute fractures which cross-cut the zoning in the plagioclase. The carbonate and chlorite (?) are not present in sufficient quantities to be detected by X-ray.

Recognition of this alteration type is based on the presence of zoned plagioclase crystals with a hard grey rim and a soft green core which locally may show white 'specks' that swell on exposure in air, and on the presence of K-feldspar which has not been attacked.

(c) Moderate Kaolinization — Moderately kaolinized quartz monzonite has the same relative properties of minerals as the weakly kaolinized rock. Accessory minerals are also the same. K-feldspar is not attacked and the mafic component is either black or chloritized biotite. The 'plagioclase' has completely broken down and is either a soft homogeneous pale green or white mixture of clay minerals. X-ray analysis indicates only the presence of kaolinite and sericite.

In thin section, the soft white or homogeneous pale green 'plagioclase' shows sericite, kaolinite, carbonate (calcite (?)), and chloritic material in a pattern which resembles the relict core described for the weak kaolinization. As the degree of alteration is relatively more intense, the hard rim is now seen as a kaolinite-rich band which surrounds the above-described altered core. Sericite flakes have not been observed in this kaolinite replacement of the original plagioclase rim. Biotite may be sagenitic, and there are generally minute rutile grains clustered around the periphery of the biotite flakes.

Recognition of this alteration type is based on the presence of unattacked pink K-feldspar and the complete breakdown of plagioclase.

(d) Intense Kaolinization — Intensely kaolinized quartz monzonite contains quartz (30%), pale bleached 'K-feldspar' (30 - 35%), pale greenish or whitish areas (originally plagioclase) (30 - 35%) and fresh black to bleached biotite (0 - 5%). Accessory minerals are apatite, zircon and sphene (?). Either magnetite or powdery hematite and/or pyrite may be present in trace amounts. Petrographic and X-ray analysis indicate that the original plagioclase has completely broken down to kaolinite and sericite and that the residual K-feldspar has been replaced by kaolinite and a little sericite.

Some whitish (originally plagioclase) material occurs within a greenish area (also originally plagioclase) and adjacent to bleached pink orthoclase. X-ray patterns of both types of altered plagioclase are identical. Petrographic evidence indicates a greater amount of very fine grained biotite plates in the white kaolinite-rich plagioclase pseudomorphs relative to the greenish plagioclase pseudomorphs. This suggests that iron, which may impart a greenish colouration to kaolinite in one case, has been fixed in biotite in the other case and consequently the coexisting kaolinite is white. This agrees with the coexistence of secondary biotite with kaolinite in the intensely kaolinized rocks.

Recognition of this alteration type is based on the presence of completely altered plagioclase and noticeably attacked K-feldspar.

B. Vein Mineralogy

Relatively few metallic minerals are present in the orebody. Molybdenite, magnetite and pyrite are the most abundant. There are trace amounts of chacopyrite, bornite, scheelite and specularite. Bornite and specularite are less abundant than chalcopyrite.

Two types of molybdenite mineralization occur within the orebody. The most prominent mineralization is the 6-inch- to 4-foot-wide continuous quartz vein with characteristic ribbons of molybdenite. Some molybdenite occurs as very finely divided grains within the quartz veins. The second type occurs as fine fractures filled with quartz-molybdenite in the form of a stockwork adjacent to and surrounding the major quartz veins. This zone of stockwork forms a halo to economic mineralization around the major quartz veins and may range in width from 20 to 200 feet.

The appearance and magnetic susceptibility of magnetite in quartz-magnetite veins varies with depth. Near surface, 'magnetite' is termed 'powdery hematite,' as it has a red streak, is non-magnetic and gives only hematite peaks on an X-ray pattern. With depth, powdery hematite becomes weakly to strongly magnetic and the colour and streak change simultaneously from red to brownish black or black. A polished section of a black magnetite with a brownish streak showed that very fine hematite grains occur along unoriented fractures within the magnetite. Iron has been dissolved as ferrous iron and oxidized to insoluble ferric oxide or hematite. A reaction of the following type is thought to occur:

$$2Fe^{++} + \frac{1}{2}O_2 + 2H_2O = Fe_2O_3 + 4H^+.$$

This variation in the magnetite with depth suggests that the development of hematite is secondary and is probably related to a Tertiary erosion surface.

Table I — Showing Relative Ages of Veins and Envelopes

The following notation is used: Qu — quartz; K-spar — K-feldspar; Bio — biotite; Ser — sericite; Mo — molybdenite; Mag — magnetite; Py — pyrite; Cpy — Chalcopyrite; Bn — bornite; Spec — specularite.

Stage	Vein	Envelope
1 (oldest)	Qu, Qu-Mo Qu-Mag (± Py)	(a) K-spar (b) K-spar-Bio., (c) Qu-K-spar-Bio- (minor altered plagioclase)
2	(Qu-Mo minor K-spar)	(Qu-Ser-Py) ((?))
	Qu-Mag	Qu-Ser-Py
	Qu-Mo	Qu-Ser-Py
	Qu-Mag-Mo (all ± Py, Cpy, Bn)	Qu-Ser-Py
	Qu-Py (± Mo, Mag)	Qu-Ser-Py ((Pyrite Zone))
3*	Qu-Mo Qu-Mag Qu-Mag-Mo (± Py, Cpy)	((No Envelopes))
4*	Qu-Py	((No Envelopes)) (Occasionally, may have 'bleached halo' around veins)
5	Spec, minor Qu Calcite Chalcedony	((No Envelopes))
6 (youngest)	Late unfilled fractures	

*Barren quartz veins may also occur with Stages 3 and 4.

Quartz-specularite veins, which are a late feature in the development of the Endako stockwork, are distinct and have an entirely different origin.

Chalcopyrite in the larger quartz-molybdenite veins generally occurs with pyrite and magnetite. Specks of bornite are rare, but when observed they occur on fractures near chalcopyrite.

C. Age Relations of Vein & Alteration Types

A sequence of relative vein ages and alteration types has been determined from numerous observations of cross-cutting relationships in logging drill core and in mapping the open pit (see Table I). The various stages outlined in Table I are superimposed on each other, with their net result being the Endako stockwork. Five to seven individual cross-cutting features may be present in a single hand specimen.

The following type of observation is the basis for Table I. A quartz-molybdenite vein with a K-feldspar envelope may be intersected by a quartz-molybdenite vein with a quartz-sericite-pyrite envelope without any offset. The relative age can be deduced because the introduced K-feldspar of the first envelope has been replaced by sericite at the intersection area of two veins. The problem of geometry of zoned alteration around central veins or fractures has been discussed by Meyer and Hemley (1967, pp. 180-183).

Three K-feldspar-bearing envelopes are shown in Stage 1. There does not appear to be any correlation between a specific type of envelope and the vein mineralogy. Similarly, there is no apparent correlation between specific vein minerals and seritic envelopes. However, within the orebody, the following generalization is true: K-feldspar-bearing envelopes are more commonly developed on quartz-molybdenite veins and sericitic envelopes are more commonly developed on quartz-magnetite veins. The presence of magnetite and molybdenite with both envelope types points out that a sulphur-oxygen fugacity ratio has played an integral role in the mineralization history.

The width of the envelopes does not appear to bear any relation to vein width and/or vein mineralogy. For example, a 1-inch K-feldspar envelope can occur on a ⅛-inch quartz-molybdenite vein as often as a ¼-inch K-feldspar envelope can occur on a 1-inch quartz-molybdenite vein. The width of the envelope is dependent on the length of time that the original fracture was open to the altering and mineralizing fluid. Maximum envelope width recorded is 8 inches.

There are a few quartz-molybdenite veins which contain pink K-feldspar and which have quartz-sericite-pyrite envelopes. Their relative position in Table I is not accurately known. They are grouped with the other examples of sericitic envelopes and are thought to be transitional between Stages 1 and 2.

A 200- to 500-foot zone rich in pyrite occurs along the south side of the orebody. Within this zone, sericitic envelopes up to ½ inch thick are developed on quartz-pyrite (± molybdenite and/or magnetite) veins, but within the orebody sericitic envelopes are developed on quartz-magnetite-molybdenite (± pyrite) veins.

The stockwork must have been under tensional stress during the formation of the large rich quartz-molybdenite veins without envelopes (Stage 3). These veins have been reopened several times to allow the precipitation of as many as twenty-one individual molybdenite ribbons over a width of approximately 8 inches. Assuming that two ribbons were formed along the walls during each fracture period, there would have been a minimum of ten fracture periods in the formation of a vein of this type.

Quartz-pyrite veins without sericitic envelopes in the orebody and pyrite zone occasionally have a 'bleached halo' with a width of up to ½ inch. There is no difference in rock texture within the halo, but the following features can be noted: (1) biotite is not present; (2) altered greenish plagioclase in the rock has turned white; (3) pink or salmon pink K-feldspar may be present; and (4) the accessory mineral is pyrite within the halo and an iron oxide outside. This suggests that within the halo Mg and Fe have been leached as biotite has been removed, altered plagioclase has been bleached white and Fe has been sulphidized and fixed as pyrite. These halos are of minor abundance and cannot be shown as a separate stage in Table I.

There is no correlation between the intensity of pervasive alteration and the vein mineralogy. However, within the stockwork, the most commonly encountered alteration type would lie between weak and moderate kaolinization. Therefore, in general, the pervasive alteration type outward from Stage 3 or 4 vein or Stage 1 or 2 envelope will range from weak to moderate kaolinization.

It is doubtful if there is any alteration effect on the quartz-monzonite due to the veins or fractures of Stages 5 or 6. A few quartz-specularite veins were observed within an intensely kaolinized shear zone, but, because, the vein was not broken, it may have followed a previously developed shear. Calcite occurs as late veins, as open space fillings (calcite rhombs up to 1 inch) and as a breccia matrix to quartz-molybdenite veined and altered quartz monzonite. Chalcedony may be found with the calcite.

D. Chemical Controls

The question of chemical control would depend on the method that Time 1 conditions were changed to Time 2 or Time 3 conditions (see *Figure 1*). K-feldspar envelopes were developed earlier than sericite envelopes, as seen by cross-cutting relations where sericite has replaced the introduced K-feldspar. Outward from these envelopes and outward from the Stage 3 and 4 veins, the rock has been pervasively kaolinized. Textural evidence indicates that the kaolinization must have developed during the formation of the veins with and without envelopes. Late veins and fractures of Stage 5 and 6 are considered to be post-alteration and, consequently, are not part of this discussion.

The interrelationship of K-feldspar-bearing envelopes, sericite-bearing envelopes and pervasive kaolinization is discussed by Hemley (1959) and Hemley and Jones (1964). The suggested mechanism is a progressive ion leaching or migration of Ca^{++}, Na^{+}, Mg^{++}, Fe^{++}, and Fe^{+++} toward the vein with simultaneous migration of K^{+} and H^{+} outward from the vein. H^{+} and K^{+} would diffuse into the rock in response to concentration gradients from the vein. The K^{+}/H^{+} activity ratio would then vary outward from the vein in some non-linear manner which is dependent on the rate of supply of heat, K^{+} and pH and on the rate of removal of leached constituents. Iron may not be removed in the case of the K-feldspar-biotite or quartz-sericite-pyrite envelopes, where the iron is

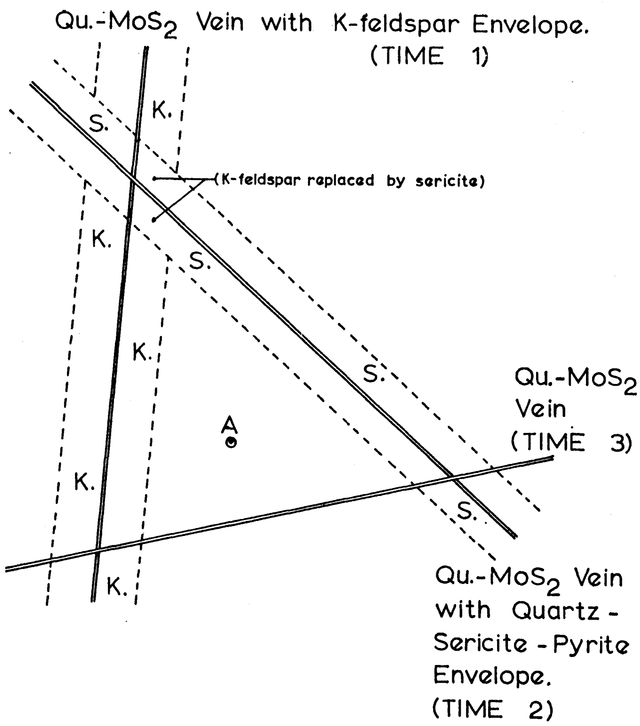
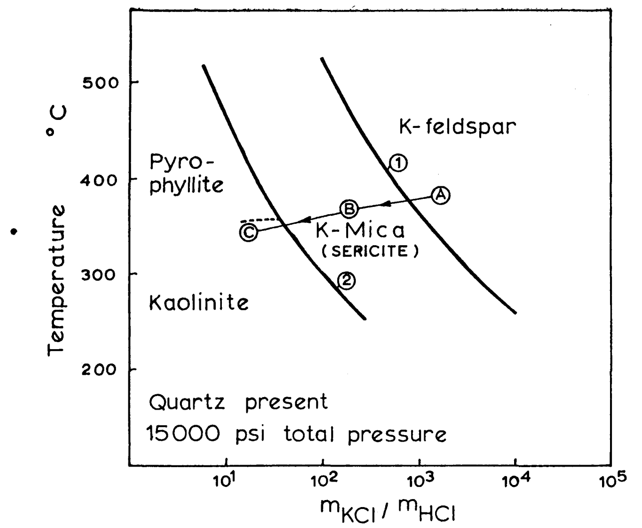


Figure 1.—Diagram illustrating time relationships of major veining events during mineralization. (Host rock is pervasively altered outward from veins with or without envelopes.)

fixed in the biotite or sulphidized to pyrite respectively. Using this concept of two-way migration and fixation, the development of K-feldspar and sericite-bearing envelopes and the absence of an envelope can be explained by the same chemical control.

From the experimental work of Hemley (1959) *(Figure 2)*, the mechanism could be either temperature or the activity ratio of K^{+}/H^{+}. Temperature must have changed between Time 1 and Time 3 conditions, but it is possible that the temperature difference was not great. Consider a case, such as shown in *Figure 1*, where a quartz-molybdenite vein is imposed on a quartz-molybdenite vein with a quartz-sericite-pyrite envelope which has been imposed on a quartz-molybdenite vein with a K-feldspar envelope. Temperature variation from the vein with the K-feldspar envelope would have to be in the order of 100°C over perhaps an inch. A gradient of this magnitude is unlikely, but it is concluded that some temperature change occurred between Time 1 and Time 3. The major control is more logically assigned to variations in the activity ratio of K^{+}/H^{+}.

Using Hemley's curves, it is suggested that for Stage 1 veins with K-feldspar envelopes, the activity ratio of K^{+}/H^{+} at Time 1 must have been in the K-feldspar field. K-feldspar adjacent to these veins has completely changed the mineralogy and texture of the original rock. At some later time (Time 2), the activity ratio was within the K-mica (sericite) field as sericite replaces the earlier hydrothermal K-feldspar. The K^{+}/H^{+} ratio would further decrease with time (Time 3) and would move into the field of kaolinite. The K^{+}/H^{+} ratio will also decrease outward from veins with or without envelopes. This latter mechanism is the cause of the pervasive kaolinization.



Circled numbers relate curves to following equations:

$3/2KAlSi_3O_8 + H^+ = 1/2KAl_3Si_3O_{10}(OH)_2 + 3SiO_2 + K^+$, (1)
(K-feldspar) (sericite)

$KAl_3Si_3O_{10}(OH)_2 + H^+ + 3/2H_2O = 3/2Al_2Si_2O_5(OH)_4 + K^+$. (2)
(sericite) (kaolinite)

Figure 2.—Reaction curves for the system K_2O-Al_2O_3-SiO_2-H_2O. After Hemley (1959). (Line A-B-C is explained in text.)

The general trend in the change of the activity ratio with time is illustrated by line A-B-C *(Figure 2)*. Point A would represent the Stage 1 veins and the development of K-feldspar envelopes at Time 1; point B would represent Stage 2 veins and the development of sericitic envelopes at Time 2; and point C would represent the development of Stage 3 veins without envelopes. The slope of line A-B-C would necessarily be low and positive because the temperature difference would be small. Absolute location of the trend line is unknown because the temperature at point C is unknown. Point C must be below the pyrophyllite field (about 350°C), as pyrophyllite is absent. Consequently, this line indicates only the generalized trend in chemical change during mineralization.

Several other possible variables may be important in this system, but their individual role is not fully understood. The activity of silica has been reported by Fournier (1967) to be responsible for the coexistence of the K-feldspar-kaolinite pair. At Ely, Nevada, Fournier reported that plagioclase broke down to a mixture of hydrothermal K-feldspar and kaolinite at low temperature and high silica activity at 1,000 bars. At Endako, K-feldspar may replace altered plagioclase within K-feldspar-bearing envelopes, but the K-feldspar-kaolinite pair are not observed to be a breakdown product of plagioclase. This is in agreement with Meyer and Hemley (1959), who suggest that K-feldspar was metastable at the time of formation of kaolinite in the argillite zone at Butte, Montana.

The partial pressure of sulphur and oxygen are important controls in this system, because sulphides (molybdenite and pyrite) as well as an oxide (magnetite) exist in the veins. Meyer and Hemley (1967) note a strong correlation between hydrogen metasomatism and the fugacity of sulphur in ore mineral assemblages and state that "strong hydrogen metasomatism exists only when the S/O fugacity ratio is relatively high, not merely when oxygen fugacity is high" (p. 222).

SUMMARY AND CONCLUSIONS

Three characteristic alteration features of the Endako quartz monzonite within the Endako molybdenum deposit are: (1) K-feldspar-bearing envelopes, (2) quartz-sericite-pyrite envelopes and (3) pervasive kaolinization. Quartz-molybdenite (minor magnetite) veins with K-feldspar-bearing envelopes are more common within the orebody than quartz-magnetite-molybdenite veins with quartz-sericite-pyrite envelopes. Pervasive breakdown of the original plagioclase to kaolinite and some sericite occurs on the outward side of the envelopes and adjacent to quartz-molybdenite veins without envelopes. Kaolinization imparts a characteristic greenish hue to the original quartz monzonite. Cross-cutting relations indicate a relative age sequence among the various alteration stages which is in agreement with a chemical control based on the activity ratio of K^+/H^+ in a nearly isothermal environment.

The relative vein sequence of hydrothermal alteration products is illustrated more distinctly at Endako than in many of the porphyry copper deposits. The change in silicate mineralogy with time can be satisfactorily explained in terms of the chemical controls, as outlined by the experimental work of J. J. Hemley. It is hoped that more descriptions of mineral deposits will be published which stress the variation of silicate and metallic mineralogy with time during mineralization so that experimentalists may more closely approximate natural alteration assemblages in their laboratory investigations.

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