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METALLIZATION AND POST-MINERAL HYPOGENE ARGILLIZATION, LOST RIVER TIN MINE, ALASKA¹

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ABSTRACT

The Lost River tin and tungsten deposit occurs in a buried granite pluton and in associated rhyolite dikes that intrude Paleozoic limestone. The dikes and parts of the granite were greisenized and then argillized irregularly. Metallization accompanied greisenization rather than argillization, although both processes probably were closely related in time.

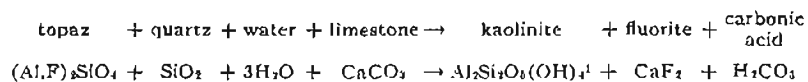
Iron-zinc ratios in sphalerite indicate that the ore minerals were deposited at a temperature between 425° C and 740° C. This temperature is within the range of the temperatures at which topaz, a common associate of the ore minerals, has been synthesized in the laboratory. The temperature of deposition of the ore minerals is above the temperature interval in which clay minerals are stable. Thus, clay minerals could not have formed

¹ Publication authorized by the Director, U. S. Geological Survey.

To Jim Williams with regards
Pete Sainsbury

while ore was being deposited. As temperatures fell and entered the stability range of the clay minerals, argillic alteration encroached upon greisen ores and wall rocks.

Reaction rims between quartz and topaz indicate that kaolinite could have formed according to the following reaction:



The clay minerals, which formed from diverse rock types, consist of kaolinite, dickite, mixed-layered chlorite-montmorillonite, and minor montmorillonite, accompanied by variable amounts of muscovite and zinnwaldite. The dickite is most common in and near late veins that cut the earlier-formed greisen.

Temperature is believed to be the principal agent governing the relations between ore deposition and argillization. Similar relations are to be expected in other high-temperature deposits where abundant veining and fracturing indicate that wall rocks reached an isothermal condition above a maximum temperature of 480° C during ore deposition.

INTRODUCTION

THE argillized rock at Lost River mine was studied through detailed mapping underground and by the separation and identification in the laboratory of sufficient samples of clay to establish the general mineralogy of the clays. The results warrant discussion because of the clear-cut independence of argillization and metallization, and because of their bearing on questions raised in some of the many recent papers on hydrothermal alteration (especially 49, 37, 30, 7, 2). The relations at Lost River apparently are similar to those described from Cornwall-type cassiterite deposits in many parts of the world, and the same sequence of metallization followed by hypogene argillization probably is repeated at many places (especially 61).

The main purposes of this paper are to record the time and space relations at Lost River and to emphasize the importance of temperature as a controlling factor in high-temperature alteration. In many cases cited in the literature, the temperature of deposition of the ores is inferred from the minerals in the associated argillized rocks. In too few cases has the temperature of deposition of the ore minerals been first determined, and the argillic products then discussed in relation to that temperature. The writer feels that inferences regarding the temperature of ore deposition that are based upon the associated argillic alteration minerals may often rest on tenuous grounds, and may be analogous to offering the theorem as proof of itself.

By use of pressure bombs, many workers have investigated in the laboratory the formation and stability ranges of the minerals commonly found in argillic alteration (41, 24, 25, 26, 18, 48, 47, 8, 40), and the results of these investigations are exerting a strong influence on interpretation of the processes of hydrothermal alteration. Recent laboratory studies that more closely duplicate hydrothermal systems than pressure-bomb experiments have been made by other workers (42, 21, 39, 25, 27). Field studies of natural springs

¹ Kaolinite formula as suggested by Dr. H. S. Yoder of the Geophysical Laboratory of the Carnegie Institute.

have been of great value in correlating laboratory results with field interpretation (14, 19, 59, 64).

General studies correlating alteration and metallization have been made throughout the world, and a substantial literature on the subject has accumulated. The common world-wide occurrence of types and suites of alteration products is apparent. Conversely, some major differences are evident, especially in the interpretation of the time relations between metallization and alteration, as is well shown by the papers of Sales and Meyers (49, Lovering et al. (37) and Tooker (60). Sales and Meyer conclude that argillization at Butte, Montana, developed simultaneously with ore deposition from ore-forming fluids that did not change noticeably in composition at the source. Lovering postulates that in the East Tintic district, Utah, different argillic phases predating ore were formed by "surges" of hydrothermal fluids of notably different composition. Tooker concludes that the argillization at Central City, Colorado, was premineral.

Lindgren (35) pointed out as early as 1915 that kaolinite could not form above 470° C. Roy and Osborne (47) established 405° C as the upper stability limit for kaolinite, nacrite and dickite. The present writer believes that more thought should be given to the upper limiting stability range of the clay minerals in discussions of argillic alteration associated with mesothermal and hypothermal ore deposits. Such deposits include the cassiterite-type tin deposits, the pyrometasomatic deposits, and possibly the disseminated deposits found in the igneous rocks with which they are genetically associated, as, for instance, the porphyry copper deposits.

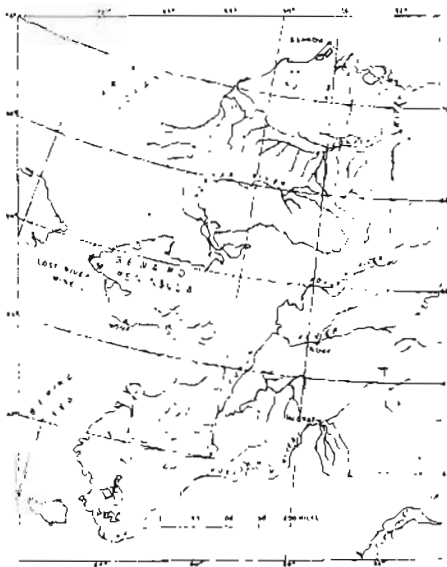


FIG. 1. Index map of western Alaska, showing location of Lost River mine.

GEOLOGY

Regional Geology

Lost River mine is near the western tip of the Seward Peninsula, Alaska, approximately 90 miles northwesterly from Nome (Fig. 1), in the York Mountains. The bedrock of most of this part of the Seward Peninsula consists of Paleozoic limestones intruded by granite stocks and both felsic and mafic dikes. The Lost River deposit is at the southern margin of a distinct metallogenetic province where cassiterite is associated with granite plutons widely spaced over an area of several hundred square miles (31, 57, 58).

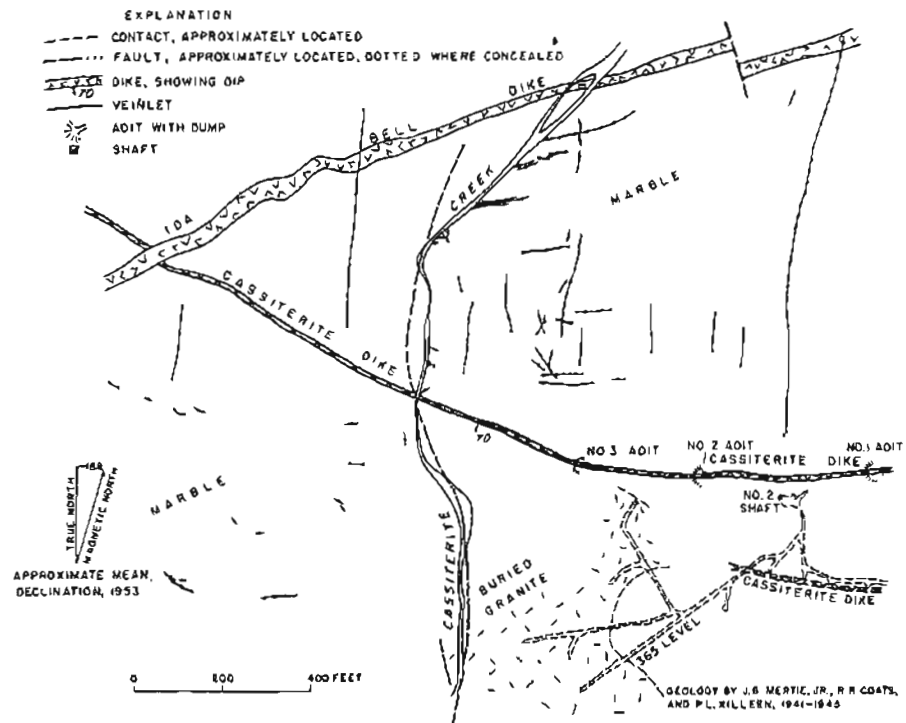


FIG. 2. Geologic map of Lost River mine.

THE ORE DEPOSIT

The deposit at Lost River is a cassiterite-wolframite deposit associated with a granite pluton that intrudes the limestone, and with basaltic and rhyolitic dikes spatially associated with the granite. The granite does not crop out, but is penetrated by exploratory mine openings driven from the main workings, which lie along an altered rhyolite porphyry dike. The deposit that has been explored consists of two ore zones: a main ore shoot localized along a rhyolite porphyry dike, named the Cassiterite dike, near its intersection

with a second rhyolite porphyry dike named the Ida Bell dike; and a surrounding zone of low-grade ore in the granite pluton and in the veined and met-somatized marble overlying the granite. No dikes have been found in the granite, and the granite has intruded at least one of the basaltic dikes. The relations indicate that the dikes are pregranite. The geology at the mine is shown in Figure 2.

The configuration of the main tin ore shoot is shown in Figure 3, which is a longitudinal projection along the Cassiterite dike. The tungsten-rich ore lies beneath the tin ore shoot. All the ore mined to date has come from the Cassiterite dike. The main ore mineral is cassiterite, which is in tactite that

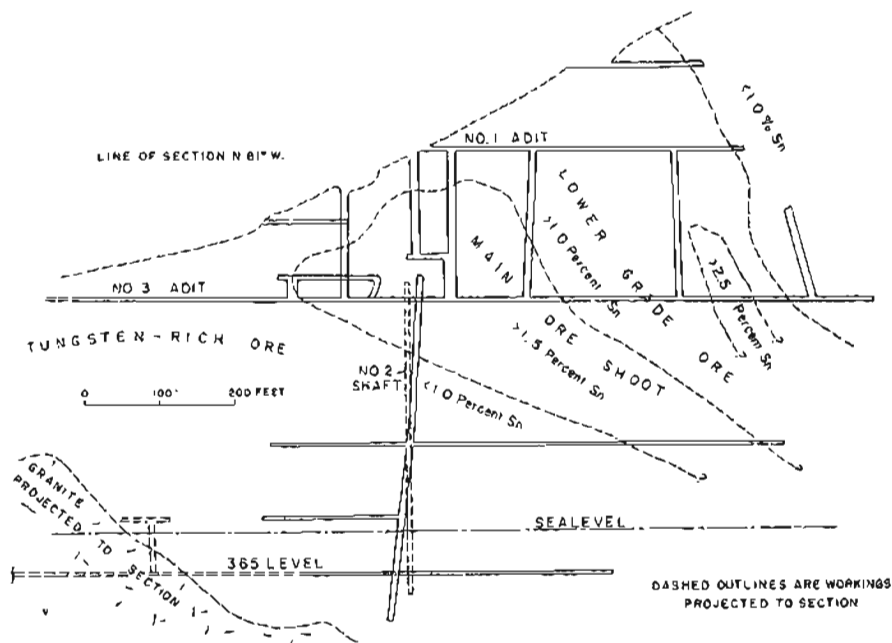


FIG. 3. Longitudinal projection, Lost River tin mine, showing main ore shoot.

is localized along planes of weakness such as dike walls, in small veinlets that cut granite, dike, and marble, and disseminated in greisenized dike rock and granite. Other identified minerals are wolframite, arsenopyrite, pyrite, galena, ferroan sphalerite, chalcopryrite, molybdenite, stannite, bismuthinite, stibnite, scheelite, pyrrhotite, hematite, ilmenite, magnetite, rutile, phenacite, beryl, and chalcocite. These minerals are herein referred to collectively as ore minerals. The main gangue minerals are quartz, topaz, fluorite, tourmaline, zinnwaldite, muscovite, garnet, calcite, siderite, hornblende, pyroxene, plagioclase, gypsum, and the various clay minerals discussed under "alteration."

Thus the Lost River deposit is seen to be a typical high-temperature tin-

tungsten deposit of the Cornwall type, but with limestone wall rocks, and an associated argillic phase.

Sequence of Geologic Events at Lost River

The sequence of geologic events at Lost River is believed to be as follows:

- (1) Regional faulting of the Paleozoic limestone.
- (2) Injection of dikes along normal faults.
- (3) Intrusion of the granite pluton.
- (4) Renewed faulting along older faults that shattered some of the dikes, and possibly parts of the granite.
- (5) Intense pneumatolytic activity at temperatures above 425° C (the minimum temperature at which the ferroan sphalerite could have been deposited), with accompanying greisenization and metallization of shattered dikes, and parts of the granite. Veins formed along fractures in the limestone.
- (6) Continued fracturing during the pneumatolytic stage with some movement localized along the Cassiterite dike to form veinlets oriented parallel or subparallel to the dike. Greisen previously formed was cut by younger greisen veinlets.
- (7) Probable sealing of most fractures.
- (8) Falling temperature.
- (9) Renewed deformation to open channels that did not coincide exactly with those that were open during metallization.
- (10) Hydrothermal activity at low to moderate pressures, and at temperatures below an absolute maximum of 480° C (the maximum temperature at which a clay mineral has been reported stable (48)), with accompanying argillic alteration of much of the greisen, marble, and tactite without recognizable deposition of ore minerals, but with some modification of pre-existing sulfide minerals, particularly iron sulfides.
- (11) Renewed faulting along the normal fault occupied by the Cassiterite dike, and probably along other faults.
- (12) Cooling.
- (13) Minor faulting along the fault occupied by the Cassiterite dike.

ALTERATION

Alteration at Lost River comprises two distinct types: greisenization of granite and rhyolite, with concomitant formation of tactite from marble, and complex argillic alteration.

Greisenization

Greisenization was most intense along the Cassiterite dike and within a restricted part of the granite pluton. The dike was greisenized so completely that no fresh dike rock has been found in any of the existing mine openings. The dike rock that appears freshest in hand specimen resembles a hard gray to white quartz porphyry with disseminated sulfide minerals

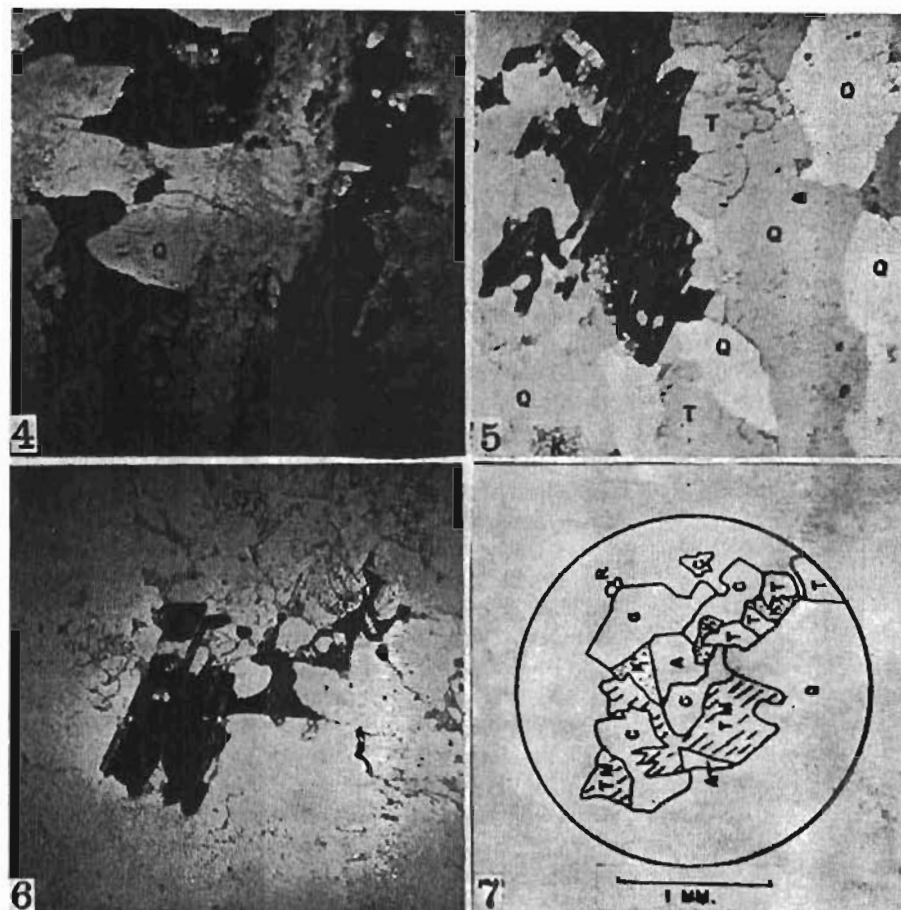


FIG. 4. Photomicrograph of greisen cut by younger greisen veinlet. Quartz, Q, topaz T, cassiterite, C. Dark areas in veinlet are tourmaline. The rock is not argillized. Uncrossed nicols.

FIG. 5. Photomicrographs of greisen with sulfide mineral retaining relict texture inherited from mica. Partly crossed nicols. Note lack of argillization. Pyrite, P, topaz, T, quartz, Q.

FIG. 6. Photomicrograph of greisen showing complex sulfide replacement of mica. Pyrite is partly replaced by younger sulfide materials. Note very faint argillization. Uncrossed nicols.

FIG. 7. Drawing from a photomicrograph of greisen showing intimate relation of sulfide minerals in a single thin section. Chalcopyrite, C, galena, G, arsenopyrite, A, rutile, R, tourmaline, TM, topaz, T, and kaolinite, K. In other sections, ferroan sphalerite, pyrite and molybdenite are found in unargillized greisen.

and cassiterite. Such rock consists chiefly of quartz and topaz and herein is called greisen although it contains less mica than the typical greisen. Some specimens contain a little mica, however. The modal composition of the greisen varies from sample to sample, but quartz generally predominates

over topaz. In samples of greisen low in sulfide minerals, white mica forms a few percent of the rock, but as the content of sulfide minerals increases, the mica decreases because of its susceptibility to replacement by the sulfide minerals. Topaz reaches a maximum of about 40–45 percent, and is a pure fluorine variety, which contains 21.6 percent of fluorine as determined by chemical analysis.¹ The greisen is cut by later veinlets of greisen, some of which are very rich in cassiterite (Fig. 4). Masses of such greisen are exposed in mine workings on the Cassiterite dike and in the underlying granite. The greisen in the dike was mined as ore, but even the richer parts of the underlying greisenized granite are of significantly lower grade when minable tonnages are considered. Much of the greisen is unargillized, but fragments of greisen are found as relicts in completely argillized rhyolite or granite.

Sulfide-bearing greisen similar to that found at Lost River is described at many of the world's tin deposits (54, 29, 28, 27, 63, 62), and presumably it is a common rock type.

The sulfide minerals in the greisen display a crude paragenetic sequence beginning with early pyrite which entered the greisen initially as a replacement of mica. This early pyrite retains a "shredded" texture inherited from the mica it replaced (Figs. 5 and 6). Other sulfide minerals replace early pyrite (Fig. 7), and such second-cycle replacement often results in the destruction of the "shred" texture. In specimens containing a large amount of ore minerals (as much as several percent), all mica is replaced. Single specimens of unargillized greisen have been found that contain almost all the ore minerals, such as pyrite, arsenopyrite, ferroan sphalerite, galena, chalcopyrite, rutile, magnetite, and molybdenite. All greisen contains several of the ore minerals. This important relation suggests that the greisen is pre-argillic and was metallized prior to argillic alteration, or that both greisen and argillized rock were pre-mineral, and the greisen was more suitable, physically and chemically, for replacement than argillized rock. Abundant megascopic and microscopic evidence supports the first conclusion. No direct evidence has been found that supports the second conclusion, and in fact the occurrence of disseminated grains of various ore minerals in some highly argillized rock refutes it.

Argillization

General Distribution.—The argillized rocks at Lost River display a complex distribution that resembles on a small scale the regional relations described for parts of the Cornwall deposits by Ussher, Barrow and McAlister (61). The Cassiterite dike was extensively argillized far beyond the limits of the commercial ore. At places, the limestone or tactite wall rocks along the dike were extensively argillized. In general, both the degree of argillization and the volume of argillized limestone increase near the granite, but the relation is not a simple one. The granite pluton also was extensively argillized, but in irregular fashion. Figure 8 shows the broad distribution

¹ Analysts: Paul W. Scott, Samuel D. Botts, U. S. Geological Survey.

of fresh granite, greisenized granite, and argillized rock on the lowest level of the mine where the pluton is intersected by mine workings.

Figures 9 and 10 depict relations exposed by mining in the upper levels of the mine on the Cassiterite dike. The important feature depicted by Figures 9 and 10 is the independence of argillic alteration and ore-bearing veinlets. Certainly the evidence is clear cut that the argillized rock is not an alteration envelope around an ore-bearing vein. Individual veinlets such as shown in Figures 9 and 10 can be traced from fresh greisen through argillized greisen at many places in the mine.

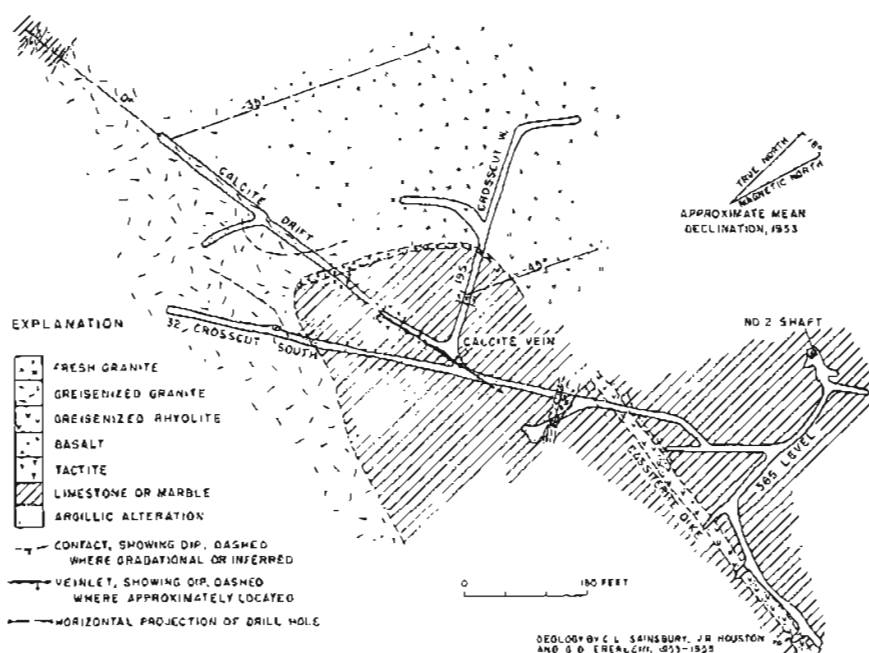
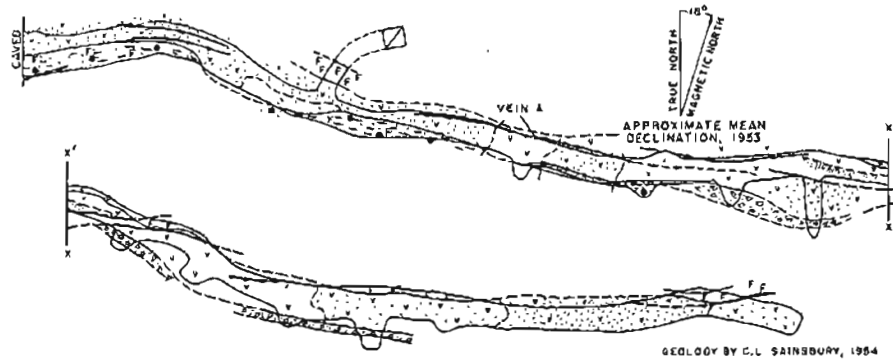












FIG. 8. Generalized geologic map, 365 level, Lost River mine, showing distribution of alteration.

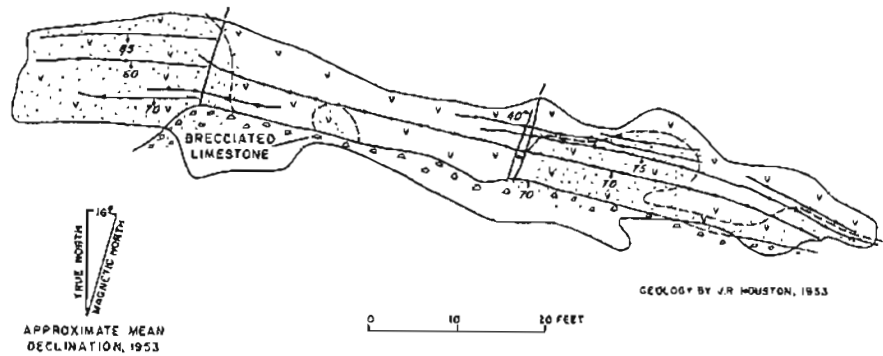
Petrography of the Argillized Rocks.—Brief descriptions are given here to show the development of argillization of three of the main rock types shown in Figures 8-10, as observed under the microscope.

The freshest granite found at Lost River is slightly altered. The granite cut by the 195 crosscut west consists of a bone-white, faintly porphyritic granite with hypautomorphic-granular texture. Its modal composition in percent is quartz, 45; oligoclase, 20; orthoclase, 30; the remainder consists of white mica, a non-pleochroic chloritic mica of very low refringence, and minor fluorite, which generally is associated with mica. Some of the white mica is faintly pleochroic in shades of brown, suggesting that it was altered from biotite. Some thin sections of granite show a grain or two of tourmaline



EXPLANATION

- | | | | |
|---|---|---|---|
|  | UNALTERED GREISEN WITH SULFIDES |  | FLUORITIZED TACTITE OR LIMESTONE |
|  | ARGILLIC ALTERATION, DOT SPACING DENOTES DEGREE |  | CLAY WITH COARSE CARBONATE (LARGE DOTS) |
|  | FAULT BRECCIA |  | LIMESTONE OR MARBLE |
-  CONTACT, DASHED WHERE GRADATIONAL OR INFERRED
 FAULT, DASHED WHERE INFERRED
 VEINLET
 IRREGULAR CLOSELY-SPACED SHEARS
- 0 20 40 FEET



EXPLANATION








- | | | | |
|---|---|---|--|
|  | UNALTERED GREISEN WITH SULFIDES |  | CONTACT, SHOWING DIP, DASHED WHERE GRADATIONAL OR INFERRED |
|  | ARGILLIC ALTERATION, DOT SPACING DENOTES DEGREE |  | FAULT, SHOWING DIP, DASHED WHERE INFERRED |
|  | FAULT BRECCIA |  | VEINLET, SHOWING DIP |
|  | LIMESTONE OR MARBLE | | |

FIG. 9 (Upper). Geologic map of No. 1 adit showing argillic alteration.
 FIG. 10 (Lower). Geologic map in A-2-E stope showing argillic alteration unrelated to veinlets.

and some of these sections show some disseminated ferroan sphalerite. No other metallic minerals are seen, and abundant assays from drill cores in this granite show that this freshest granite is almost barren of ore minerals, except where cut by veinlets.

The freshest granite is cut by thin veinlets that occupy joints and that contain ore and gangue minerals similar to those in veins in the limestone. Incipient argillization is shown by minute clots of clay minerals in the fine-

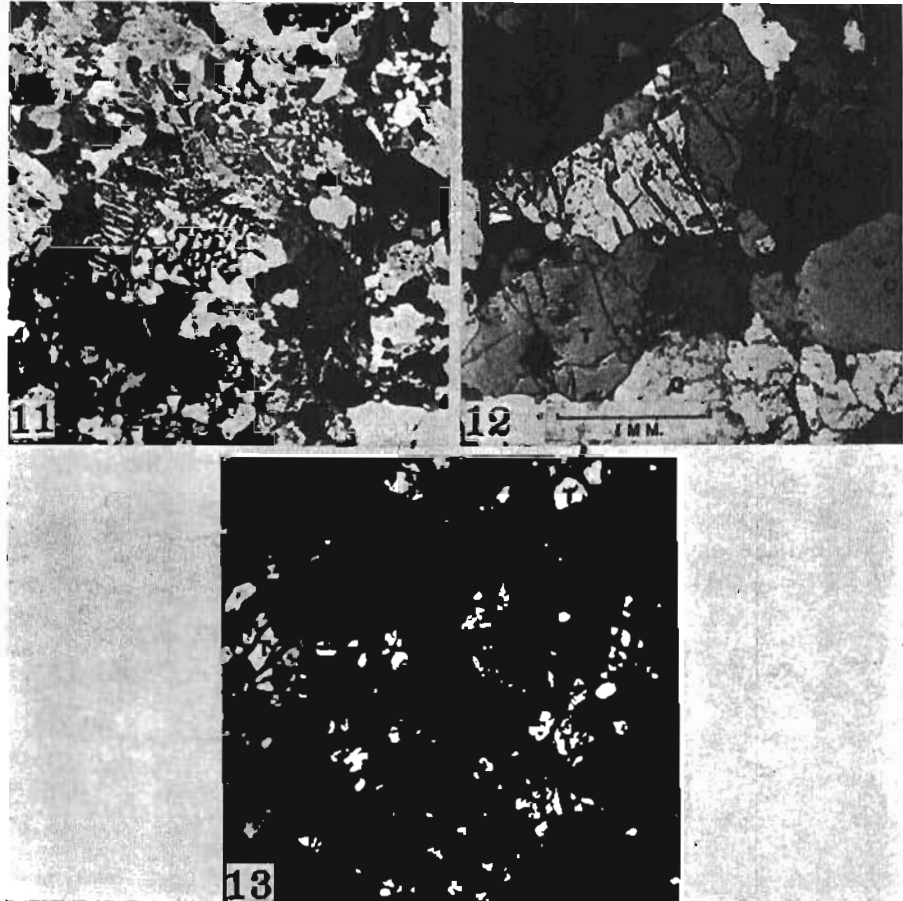


FIG. 11. Photomicrograph of freshest granite, 195 crosscut west, 365 level. Note graphic texture of large quartz grains, twinned plagioclase, and abundant solid inclusions in all minerals.

FIG. 12. Photomicrograph of greisen from 365 level showing incipient argillization. Other minerals shown are pyrite, P, topaz, T, and quartz, Q. Note argillic alteration along cleavages in topaz. Partly crossed nicols.

FIG. 13. Photomicrograph of completely argillized greisen from 365 level showing residual topaz, T, encased in mass of clay minerals, K. Dark areas are fluorite and/or sulfide minerals. Crossed nicols.

grained parts of the rock. The oligoclase and orthoclase, however, are relatively unargillized even though they contain abundant minute solid inclusions (Fig. 11).

Greisen and partly greisenized granite and rhyolite porphyry exist in all stages of argillization. With moderate argillization, the rocks are converted to a soft to friable mass of residual mineral grains encased in clays, or a mixture of clays and fine-grained mica. In general, the mica in samples of argillized granite or greisenized granite is fine-grained muscovite, but zinnwaldite is more common in samples of argillized rhyolite dike rock or greisenized dike rock.

Stages in the conversion of greisen to clay are shown in Figures 12 and 13. Argillization begins in the fine-grained parts, at grain boundaries, and along the cleavages in the topaz. With increasing argillization, both quartz and topaz are attacked, and the final product consists of clay minerals with a few scattered remnants of quartz and topaz and variable amounts of fluorite. The iron sulfide minerals (pyrite and pyrrhotite) generally are lacking in such rock, but the cassiterite, arsenopyrite, and ferroan sphalerite remain. Specks of limonite and limonite staining indicate that the original pyrite and pyrrhotite were altered to limonite.

The limestone is argillized at places to a mass of soft clay. Elsewhere, the limestone is hard to firm, and contains vugs lined with calcite, manganese calcite, and/or pale green fluorite. Dolomite was identified by X-ray diffraction in some of the clays derived from limestone. The clays derived from limestone generally are darker than those derived from granite or greisen. Stratified clay seams and slump features are apparent locally in clays derived from limestone, and probably indicate solution stoping.

It is particularly noteworthy that myriad ore-bearing veinlets cut the marble exposed by mine openings, but that a great many of these veinlets do not contain clay minerals, again offering confirmatory evidence that the argillic alteration is not a halo about veins. Other veins do contain clay minerals, but evidence is presented later in this paper to show that such veins probably mark channels that were opened recurrently during both metallization and argillization.

Clay mineralogy.—Clay minerals were separated from 38 samples taken from mine openings and diamond drill cores that explored the granite. The clay minerals were identified by X-ray diffractometer after suitable treatment. Twenty-seven of the samples were separated and identified by John C. Hathaway and Carol C. Parker, and 11 were separated and identified by the writer.

The clay mineralogy is moderately complex. A regularly mixed-layered chlorite-montmorillonite occurs in 31 of 38 samples which represent altered limestone, granite, greisen, and probably tactite. Montmorillonite was identified in four samples. Hathaway and Parker state that the mixed-layered clay is chlorite and montmorillonite interlayered in 1:1 ratio. Such regularly interstratified clay has resisted attempts at synthesis, and is believed to represent alteration of chlorite or trioctahedral mica (46).

Kaolinite and/or dickite was identified in every sample, and forms the

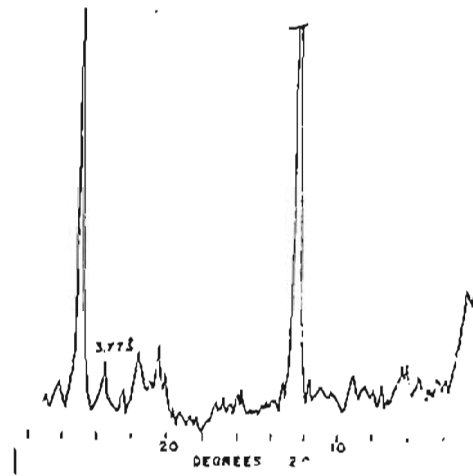


FIG. 14. Diffractometer pattern of unoriented, untreated dickite.

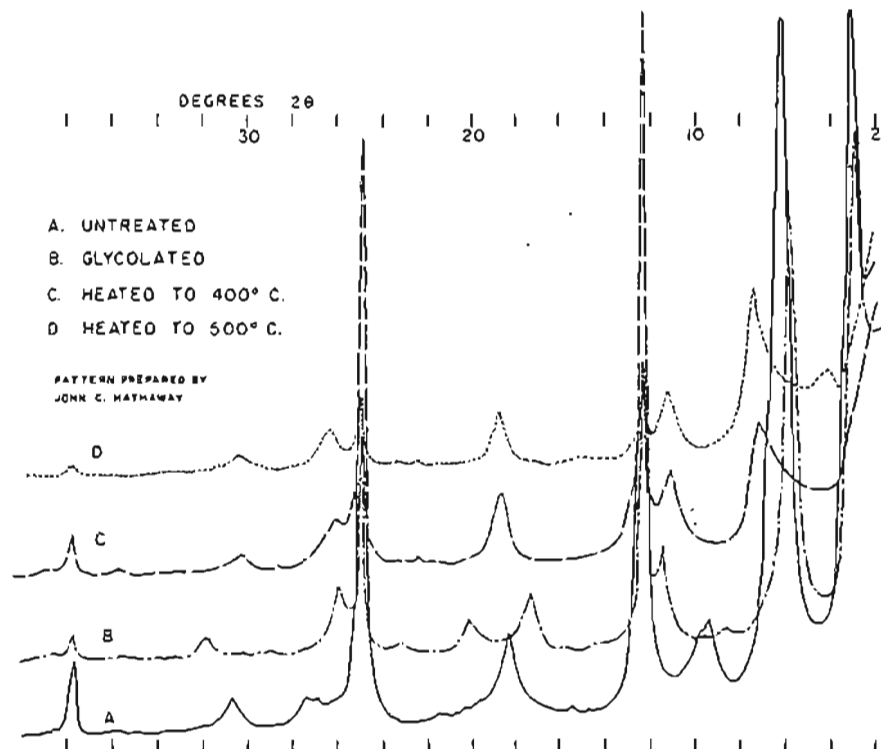


FIG. 15. Diffractometer patterns of oriented, treated kaolinite and mixed-layered chlorite-montmorillonite.

bulk of the clays. Dickite was identified positively in 14 samples representing argillized dike rock or greisen, limestone, and granite. It was also identified in a clay veinlet in limestone.

Diffractometer patterns of the clays are shown in Figures 14 and 15. The peak shown at 3.77 Å on the dickite pattern is the main one that differentiates dickite from kaolinite. The curves for the mixed-layered chlorite-montmorillonite are similar to those reported by Earley, Brindley, McVeagh, and Vanden Huevel (15).

Chemical Changes During Alteration

Chemical analyses were made of 13 rocks from the Lost River mine by P. L. D. Elmore, K. E. White, and S. D. Botts of the U. S. Geological Survey, using the rapid method (32). Fluorine was determined separately. Although chemical analyses that would have detected the minor constituents such as lead, zinc, tin, tungsten, and molybdenum would have been useful, the rapid analyses are believed to be sufficiently accurate to detect the major chemical changes that took place during greisenization and argillization. The analytical results are shown in Table 1, and the composition of 100 cc of rock is shown in Table 2. The gains and losses are shown graphically in Figures 16-19.

The method of computation used in these tables involves the conversion of weight percent of constituents to the composition of 100 cc of rock through the use of bulk density (44). This method has inherent weaknesses, as pointed out by Poldervaart (44) and others, the major objection being that it assumes a constant volume during metasomatism. Cooper (11) recently has shown the feasibility of determining volume changes, however, where dependable thickness measurements can be obtained. Accurate information on volumetric change was not obtained at Lost River. Barth (4) has proposed an alternative scheme, which assumes a constant number of oxygen ions. Discussions by Brajnikov (5), Perrin (43), Eskola (17), and others show that no petrologic calculation can be made that is free of potential error. The evidence at Lost River indicates little volume change in the granite and dike rocks, but appreciable volume changes in the limestone, at least locally. The volume changes cannot be quantitatively assessed, however. The results shown in Figures 17-19 are based upon chemical changes in the granite, and are believed to represent real changes. It should be pointed out, however, that the slopes of the curves could be manipulated substantially by alternative calculations, e.g., the exclusion of water, sulfur, or fluorine. Figure 16 shows the positions of the analyzed rocks with respect to fresh granite, high-topaz greisen, and completely argillized granite.

Chemical Changes During Greisenization.—Figure 17 depicts the chemical changes during conversion of granite to greisen containing progressively greater amounts of topaz. The underlined numbers below the vertical lines show the approximate amount of topaz in the rock. The rocks lie along the line between fresh granite and greisen that contains progressively larger amounts of topaz, as shown in Figure 16.

TABLE 1
 CHEMICAL COMPOSITION OF GRANITE, GREISEN AND ARGILLIZED GRANITE OR GREISEN, LOST RIVER MINE
 Analysts: P. L. D. Elmore, K. E. White, S. D. Botts, U. S. Geological Survey

Oxide	1	2	3	4	5	6	7	8	9	10
SiO ₂	75.73	75.00	66.50	65.50	59.80	70.80	71.90	70.60	71.00	50.90
Al ₂ O ₃	13.63	14.00	15.50	18.30	16.50	15.30	14.20	15.80	12.80	19.70
Fe ₂ O ₃	.24	.50	.00	.00	.00	1.00	.30	.50	.30	1.10
FeO	.56	2.10	2.60	2.10	4.60	1.60	1.70	1.10	2.60	.85
MgO	.19	.40	1.70	.18	.12	.38	1.00	1.50	2.10	9.30
CaO	.63	.39	.28	3.40	.30	.62	.82	.74	.98	1.20
Na ₂ O	3.47	1.10	.30	.05	.04	2.30	.43	.06	.37	.38
K ₂ O	4.70	3.00	.06	.69	.06	5.90	4.60	1.70	1.10	.76
TiO ₂	.02	.02	.02	.00	.06	.02	.02	.01	.02	.02
P ₂ O ₅	.00	.02	.02	.01	.02	.01	.01	.00	.01	.00
MnO	.11	.46	.12	.16	.11	.24	.49	1.40	.34	.16
H ₂ O	1.17	1.60	2.30	1.40	.61	1.60	3.50	4.20	7.20	14.10
CO ₂	.07	.12	.09	.08	1.20	.08	.31	.90	.26	.16
FeS ₂	—	—	6.90	3.10	11.30	—	—	—	—	—
F	.55	2.14	3.28	7.92	5.26	1.37	1.94	2.44	1.12	1.10
Sum	101.07	100.85	99.67	102.89	99.98	101.22	101.22	100.95	100.20	99.73
Less O = F ₂	.23	.90	1.40	3.30	2.20	.58	.82	1.00	.47	.46
Corr. Sum	100.84	99.95	98.27	99.59	97.78	100.64	100.40	99.95	99.73	99.27
Specific gravity	2.582	2.750	2.920	2.975	3.10	2.60	2.40	2.920	2.40	2.170
Remarks	Granite, average of 3 analyses	Partially greisenized granite, approx. 5% topaz	Greisen, approx. 18% topaz	Greisen, approx. 23% topaz	Greisen, approx. 28% topaz	Partially argillized granite, 2% residual topaz	Moderately argillized granite, 3% residual topaz	Moderately argillized granite, no residual topaz	Argillized granite, no residual topaz	Intensely argillized granite, no residual topaz

TABLE 2
COMPOSITION OF 100 CC OF ROCKS, LOST RIVER MINE

Oxide	1	2	3	4	5	6	7	8	9	10
SiO ₂	195.535	206.250	194.180	194.863	185.380	184.080	172.560	206.152	170.400	110.453
Al ₂ O ₃	35.193	38.500	45.260	54.444	51.150	39.780	34.080	46.136	30.720	42.749
Fe ₂ O ₃	.620	1.375	.000	.000	.000	1.600	.720	1.460	.720	2.387
FeO	1.446	5.773	7.592	6.248	14.260	4.160	4.080	3.212	6.240	1.845
MgO	.491	1.100	4.964	.536	.372	.988	2.400	4.380	5.040	20.181
CaO	1.627	1.073	.818	10.115	.930	1.512	1.968	2.160	2.352	2.604
Na ₂ O	8.956	3.025	.876	.148	.124	5.980	1.032	.175	.888	.825
K ₂ O	12.135	8.250	.175	2.053	.186	15.140	11.040	4.964	2.640	1.649
TiO ₂	.052	.055	.058	.000	.186	.052	.048	.030	.048	.043
P ₂ O ₅	—	.055	.058	.030	.062	.026	.024	.000	.024	.000
MnO	.284	1.265	.350	.476	.341	.624	1.176	4.088	.816	.347
H ₂ O	3.021	4.400	6.716	4.165	1.891	4.160	8.400	12.264	17.280	30.597
CO ₂	.181	.330	.263	.238	3.720	.208	.774	2.628	.624	.347
FeS ₂	—	—	20.148	9.223	35.030	—	—	—	—	—
F	1.420	5.885	9.578	23.562	16.306	3.562	4.656	7.125	2.688	2.387
Sum	260.961	277.338	291.036	305.101	309.938	262.172	242.928	294.774	240.481	216.414
Less O = F ₁	.594	2.475	4.088	9.818	6.820	1.508	1.968	2.920	1.128	.998
Corr. Sum	260.367	274.863	286.948	296.283	303.118	261.664	240.960	291.854	239.353	215.416

The analyses show significant changes. The oxides of potassium and sodium are removed rapidly with greisenization, reflecting the destruction of orthoclase and plagioclase feldspar, or its conversion to topaz, without fixation of K₂O and Na₂O in new minerals in the greisen. Silica rises sharply with initial greisenization (e.g., low-topaz greisen), and falls steadily as more topaz forms, as would be expected. The downward break in the silica curve coincides with the upward break in the curve for iron sulfide, which apparently marks the beginning of metallization. Alumina and fluorine rise steadily

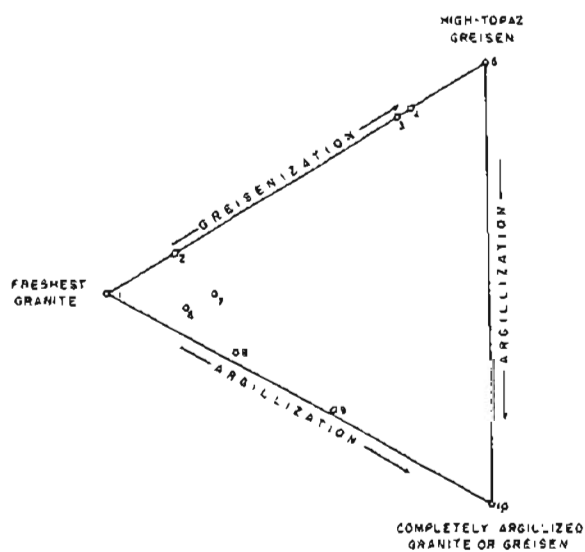


FIG. 16. Diagram showing relative positions of rocks analyzed with respect to degree of alteration.

as a direct consequence of the formation of high-alumina topaz at the expense of feldspars. Total iron, not shown as an individual line on the diagrams, increases through greisenization. The changes in the oxides of calcium, magnesium, and ferric iron are not large enough to be considered diagnostic, but trends probably are reflected.

Chemical changes involved in greisenization of granite near various tin deposits have been discussed by Vogt (62), Dalmer (13), and Cotton (12);

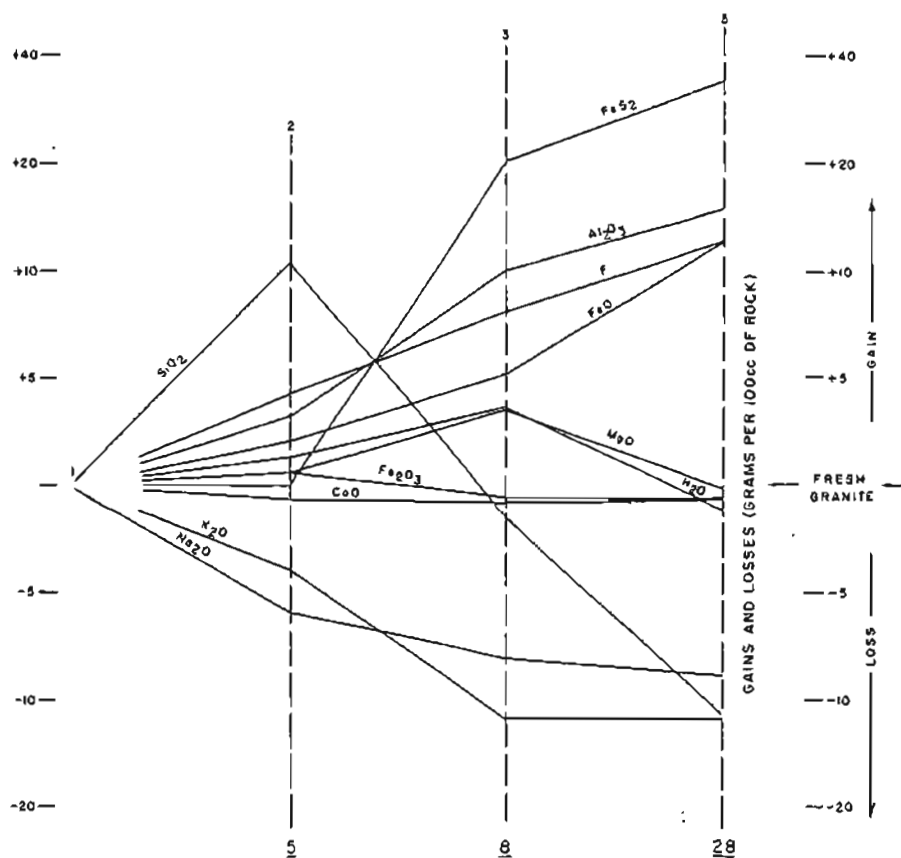


FIG. 17. Chemical changes during greisenization.

their results were summarized by Ferguson and Bateman (20). The chemical changes in converting granite at Lost River to greisen are compatible with changes observed elsewhere in regard to loss of the oxides of potassium and sodium, and gain of iron and fluorine. Alumina and silica, however, can be expected to show variable degrees of change depending entirely upon the role of topaz and mica in a greisen. In any greisen with a high percentage of topaz and a low percentage of mica formed at the expense of feldspar in a granite,

alumina will increase and silica will decrease, for conversion of feldspar to topaz involves gain of alumina and decrease of silica. This is shown in Figure 17. Lindgren (36) pointed out in 1901 that greisenization does not necessarily imply addition of silica, which is borne out by the present study.

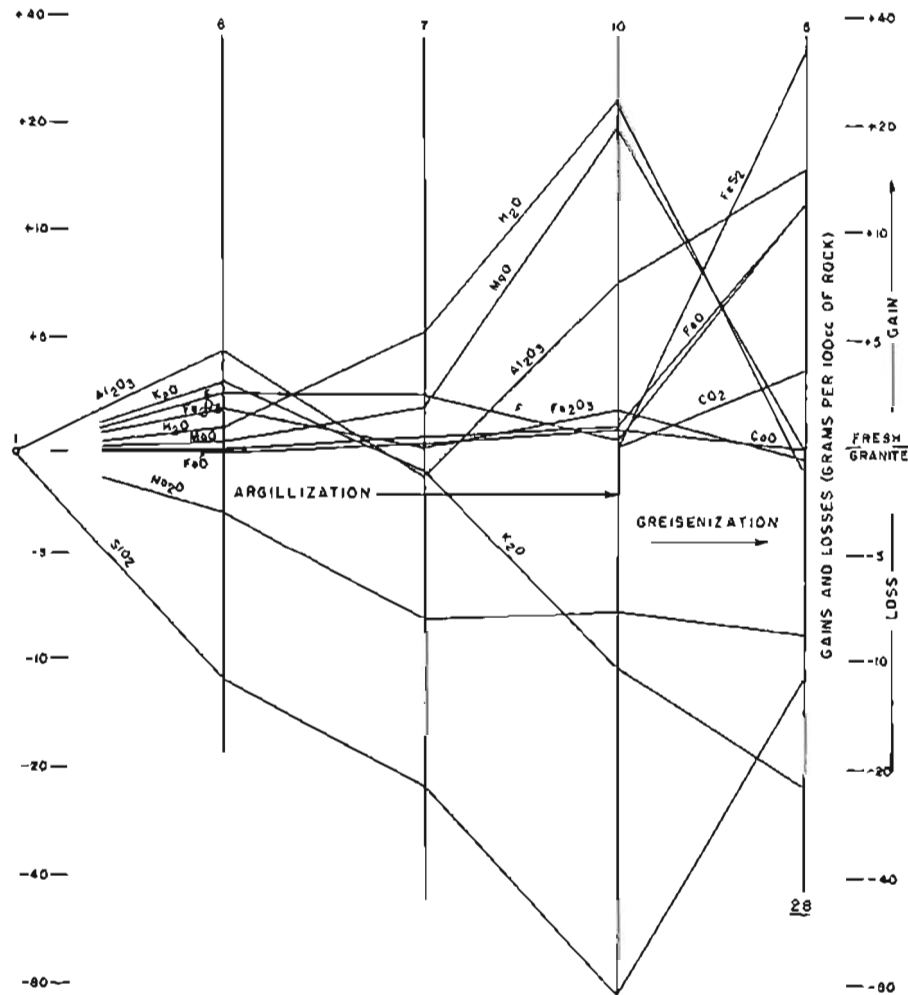


FIG. 18. Chemical changes in argillization of partly greisenized granite.

Chemical Changes During Argillization.—The chemical changes involved in argillization of partly greisenized granite are shown in Figure 18, and in argillization of ungreisenized granite in Figure 19. The curves exhibit strong resemblances to those of Figure 17 for the oxides of potassium, sodium, and silicon. Silica is leached more strongly during argillization. Water increases

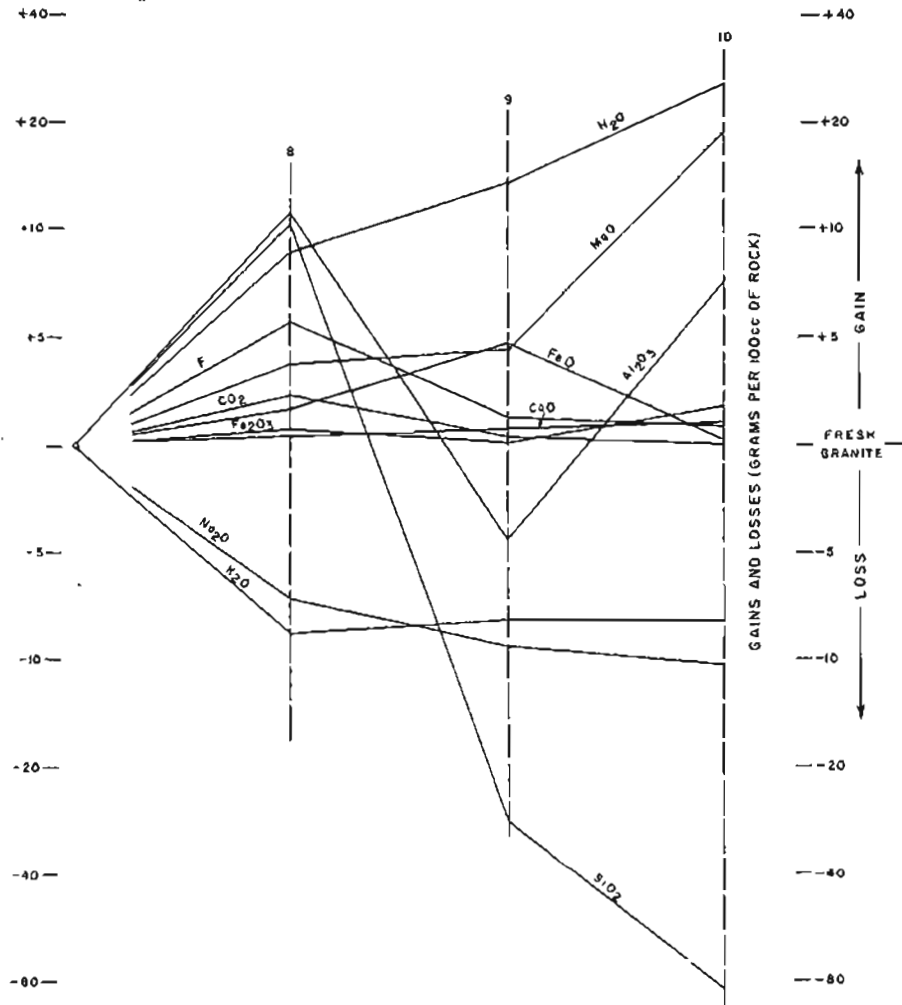


FIG. 19. Chemical changes in argillization of ungreisenized granite to faintly greisenized granite.

because of the hydrated clay minerals. The increase of magnesia probably reflects trapping of magnesium ions, derived from the limestone into which the granite is intruded, by the mixed-layered chlorite-montmorillonite or in the dolomite associated with some of the argillized granite. The absence of sulfur in argillized granite which was not strongly greisenized previously is notable (Table 1, Fig. 19), and offers confirmatory evidence that metallization and argillization were not contemporaneous. The final column in Figure 18 shows the chemical changes that would be required to convert completely argillized granite to greisen with a large percentage of topaz.

The curves depicting chemical changes show that the oxides of potassium, sodium, and silicon behaved similarly during changes that would seem to reflect a substantial change in the fluids. For instance, the fluids responsible for metallization must have carried considerable fluorine and sulfur, yet silica and the alkali oxides behaved the same as during the argillic phase of alteration when fluorine and sulfur presumably were considerably reduced. The behavior of silica and the oxides of potassium and sodium would suggest continued acid leaching, probably by carbonic acid, as Lemberg (34) has shown that topaz, normally a very resistant mineral, breaks down rapidly in carbonic acid.

DISCUSSION

Hypogene Origin of Clays

The main thesis of this paper, that argillization at Lost River is hypogene and postmineral, depends in large measure on the factors that establish the argillization as hypogene rather than supergene. Consequently, it is necessary to present that evidence here. The main points are:

(1) Supergene oxidation of sulfides at Lost River is slight even at the surface. Abundant primary sulfide minerals including pyrite and arsenopyrite are found at the surface in the Cassiterite dike and in myriad veinlets. Oxidation products of the ore minerals are known only in minor amounts.

(2) Weathering at Lost River is accomplished principally by frost action. Frost-riven fragments of dike rock containing fresh pyrite can be found at the surface.

(3) The argillized parts of the dikes are spatially associated with the parts that contain hypogene minerals, such as topaz, whereas pyrite is widespread in the dikes.

(4) The mine is within and beneath the permafrost, and the lower levels of the mine are at least 200 feet below the water table. The York Mountains were glaciated, and uplifted during the Pleistocene and Recent epochs (58), from which it is concluded that the deposit was continuously beneath the water table during any warm periods since late Pliocene. No evidence has been found to indicate that pre-Pleistocene weathering has survived to the present in the York Mountains.

(5) The amount of clay increases near the granite, which is below the water table in the lowest level of the mine. Sulfide minerals, however, are abundant throughout the mine.

(6) The large masses of clay in and near the granite are capped by marble and tactite, containing notable amounts of pyrite and other sulfide minerals, yet the tactite is not argillized except where cut by clay veinlets.

(7) Dickite is found throughout the mine, and dickite generally is believed to be most commonly a product of hydrothermal alteration (21).

(8) The breakdown of topaz suggests hydrothermal action by carbonic acid, as found by Lemberg (34), and supported by Povarennykh (45).

These eight facts seem to the writer to rule out a supergene origin for the clays.

Megascopic Evidence for Post-mineral Age of Clays

The post-mineral age of the clays is shown by petrographic evidence already presented. However, features of much larger scale were used initially to show a post-mineral age for the clays, and offer conclusive proof. Some of these megascopic features are:

(1) Veins and veinlets with no argillic envelope which transgress lithologic facies that grade from hard, gray sulfide-bearing greisen through partly argillized greisen to completely argillized greisen (Figs. 9, 10). Many of these veinlets contain topaz, mica and ore minerals, and the silicate minerals in the vein are fresh in the fresh greisen, and argillized in the argillized greisen, showing that argillization advanced "endwise" on the vein, or upward on certain parts of the vein only.

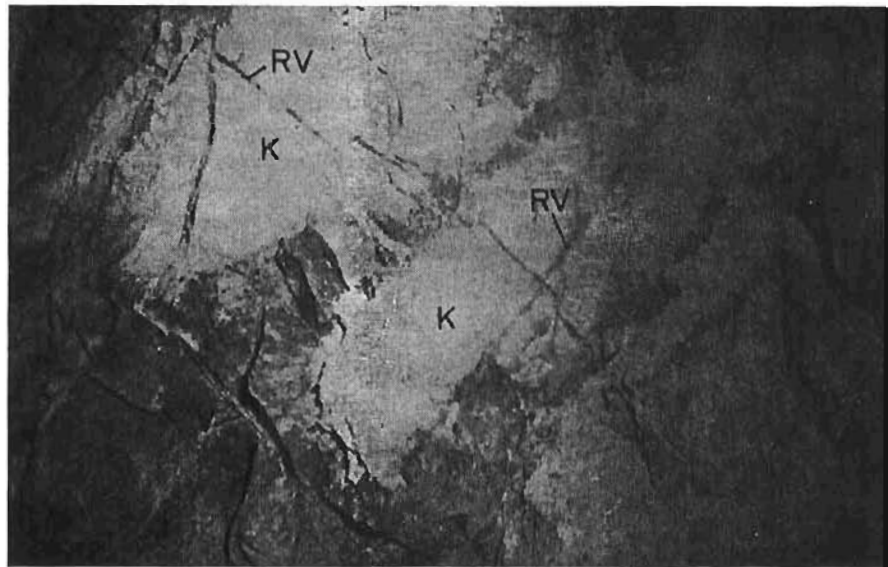


FIG. 20. Photograph of solid kaolinite, K, developing in the Cassiterite dike, No. 3 adit level. Note small, thin veinlets, V, along joints in lower left. Veinlets with diffuse outline but with same orientation are retained in clay as relict structures, RV, in solid clay. Veinlets are approximately $\frac{3}{8}$ -inch wide.

(2) Completely argillized dike rock has been found with relict veinlets containing cassiterite, arsenopyrite, ferroan sphalerite, wolframite and fluorite. The veins are oriented the same as those found in adjoining unargillized rock that contain mica, topaz, quartz, and tourmaline in addition (Fig. 20).

(3) Ore minerals are lacking in much of the granite that is highly argillized, yet ore minerals are everywhere found in unaltered greisen or in argillized rock containing residual topaz.

(4) Large volumes of the Cassiterite dike, the granite, and the limestone near the granite, consist almost entirely of massive clays that contain cassiterite

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in economic amounts. The solid white clay at the east end of No. 1 adit (Fig. 9) contains an average of 2.5 percent of tin that occurs disseminated in the clay. This argillized rock grades laterally into greisen containing tin in similar amounts but with abundant sulfide ore minerals. Such relations clearly show that the argillic alteration is later than cassiterite and greisenization.

(5) Small fragments of slightly argillized greisen are found isolated in solid clay, a relation that is common in the clay pits of Cornwall (61), where kaolinization is now considered to be hypogene (28, 6, 27). This relation can be explained reasonably only by assuming that the greisen fragments are residual. The residual greisen fragments at Lost River contain cassiterite and sulfide ore minerals, which shows clearly that cassiterite and sulfides predated argillic alteration.

(6) Veins with a center "rib" of fluorite encased in clay are found in limestone in many parts of the mine. Fluorite has spread into the walls beyond the clay. The center rib of fluorite is cut by clay-filled fractures. In near proximity are other fluorite veins with unargillized walls, again indicating some type of disparity between veins and argillic alteration.

(7) Some veins in limestone have clay-fluorite centers and walls of banded tourmaline-fluorite-sulfide rock, but are rare. Small clay veinlets branch from the centers of the veins and crosscut the banded walls. The clay is a mixture of mixed-layered chlorite-montmorillonite and kaolinite. The clay in such veins obviously is later than the tourmaline and the ore minerals.

The veins described under 6 and 7 above are believed to represent older veins that were reopened during the argillic phase of alteration, or that remained open until temperatures dropped to the point where clay minerals were stable.

Temperatures During Metallization and Argillization

Temperatures Deduced from Ore Minerals and Greisen.—Direct evidence of the actual temperature of ore deposition at Lost River is found from the iron-zinc ratios in sphalerite, according to Kullerud's method (33). The brilliant-black ferroan sphalerite is very common in the granite and in veinlets in the Cassiterite dike. R. G. Coleman, of the U. S. Geological Survey, reports an iron content of 11.7 weight percent in a sample of a single large and pure crystal that came from the 365 level. Semiquantitative spectographic analyses of two other specimens of single pure crystals showed iron in the range of 10–15 percent. The minimum temperature of deposition of the sphalerite, according to Kullerud's curves, is about 425° C, with a maximum temperature that could range up to 740° C. Abundant pyrite is associated with the sphalerite, but pyrrhotite is rarer, being found in quantity only in sulfide concentrates from the cleaner circuit in the mill flotation plant. Thus, in the absence of dependable data showing coexistence of sphalerite and pyrrhotite, the maximum temperature of deposition cannot be stated certainly. The minimum temperature of deposition, however, may be taken as 425° C without pressure correction.

Deductive evidence of the temperature of ore deposition is gained from a

consideration of the stability range of topaz, the ubiquitous associate of ore in greisen at Lost River. Topaz has been synthesized by Daubrée (14), Coes (10), and Michel-Lévy and Wyart (38): Daubrée by the action of steam on tin fluoride, and the other two by use of the autoclave. Coes reports a temperature of formation that ranges between 600–900° C, and Michel-Lévy and Wyart report synthesis at 500° C and a pressure of 4,000 kg/cm². At 455° C no topaz formed.

Tourmaline is found sparingly at Lost River in the Cassiterite dike, and in veinlets in the marble. It is less abundant in the granite, but it has been found. Tourmaline has been synthesized by Frondel, Hurlbut and Collette (22), and by Smith (56), at temperatures between 400–500° C, although neither state the upper stability range. Smith suggests a relatively restricted pH range for the tourmaline he synthesized, generally on the alkaline side but carrying over into the mildly acid range with increasing water. However, tourmaline grows authigenically (59), and therefore cannot be used as a decisive temperature indicator, although laboratory experiments suggest its hydrothermal formation would require a temperature of 400–500° C.

Cassiterite is of little value in determining the temperature of ore deposition, owing to the wide range in its temperature of formation, from surface water (wood tin) to typical tin-tungsten veins of hypothermal origin (3). Cassiterite has been synthesized by Smith (56) from room temperatures to 450° C, but the upper stability range was not determined.

From the direct and deductive evidence, it is believed that the temperature during greisenization and introduction of the ore minerals was at least 425° C, and probably was not below 500° C, the minimum temperature reported for formation of topaz. The maximum temperature of deposition could reach 740° C.

Temperatures Deduced from Clay Minerals.—Clay minerals have been synthesized in the laboratory by numerous workers. One fact of paramount importance to this paper, which emerges from experimental data, is the relatively constant upper stability limit of any clay mineral in the various systems studied, a limit that falls between 400 and 480° C. Roy and Osborne (47) report that kaolinite, halloysite, nacrite, and dickite decompose at 405° C, and 10,000 psi water pressure, and aluminum montmorillonite at 420° C. Varying the water pressure from 2,500 to 25,000 psi did not alter the decomposition temperature more than 10 degrees. Roy and Roy (48) showed that in a system containing magnesium, montmorillonite appeared at 480° C. downward. Noll (41) in pressure bomb runs at 500° C. found pyrophyllite to be the stable phase, whereas some kaolinite formed at 400° C. Sand, Roy, and Osborn (50) show a maximum decomposition temperature of 450° C for sodium-montmorillonite.

From the above it is seen that the stability ranges of the minerals formed during greisenization and metallization, particularly topaz, are either above or in the uppermost part of the stability range of the clay minerals. The conclusion based upon mapping—that the metallization preceded the argillization—is completely compatible with laboratory data. The literature demonstrates great complexity of mineral assemblages with differing chemical

environments such as pH (H^+ ion concentration), K^+ concentration, etc., but irrespective of chemical environment, no clay minerals were ever formed in laboratory experiments above the temperature limits quoted above. The writer believes that this fact has not received its proper consideration by many writers who discuss argillic alteration. Ores deposited even in the temperature range between 350–400° C may be expected to show complexity of associated argillic alteration products that may be a direct consequence of temperature differences rather than of changes in the mineralizing fluids.

Temperatures of Deposition of Tin Ores.—Smith (54) tested samples of Cornish ore by use of the decrepitation method, and found a temperature of formation in the range 265°–390° when corrected to a depth of burial of two miles. On this basis, Smith questions the existence of all pneumatolytic deposits. Hosking (27) apparently accepts Smith's conclusions as valid for the entire Cornwall district. In view of the indicated temperature of deposition of the Lost River ores, a supercritical gaseous phase is indicated, even though this gas may have been dense.

The writer thinks that the temperature of formation of cassiterite and other minerals from the Cornwall district as reported by Smith probably are in error, and should not be considered as representative of the temperatures of formation of deposits of cassiterite in greisens. The Lost River deposit is typical of deposits known the world over, and the temperature of deposition at Lost River undoubtedly was above that reported by Smith for the Cornwall deposits. The writer's investigations support the opinion long held by geologists that the tin deposits associated with granite plutons are formed at very high temperatures in the range of the "pneumatolytic" stage. The temperatures stated by Ahlfeld (1) for the deposition of the Uncia-Llallagua deposits in Bolivia seem realistic. Ahlfeld describes the following stages: (1) a high temperature, pneumatolytic phase with introduction of cassiterite and tourmaline; (2) an intermediate phase at a temperature of over 400° C, and (3) a hydrothermal, low-temperature phase. The Lost River deposit would fall into Ahlfeld's initial high-temperature, pneumatolytic phase.

Edwards and Lyon (16) have determined the temperature of deposition of sphalerite at the Aberfoyle tin mine, Tasmania. They record a temperature of deposition of "about 600° C." The relations they describe between ore minerals are very similar to those at Lost River, with cassiterite and wolframite preceding the sulfides. They do not record argillic alteration associated with the ore deposits.

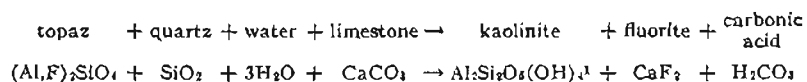
CHEMISTRY OF SOLUTIONS DURING ARGILLIC ALTERATION

A complete discussion of the chemistry of the solutions that argillized the rock at Lost River is beyond both the scope of this paper and the writer's competence. A few remarks, however, seem in order owing to the fact that topaz in large amounts was altered to clay.

Many writers have suggested that an acid environment contributes to the formation of kaolinite (23, 26, 30); Smith (54) synthesized cassiterite from alkaline solutions, and concluded that cassiterite possibly is deposited from

acid gaseous solutions in near-surface environments and from alkaline solutions under deep-seated conditions.

The work of Lemberg (34) and Povarennykh (45) that demonstrates the instability of topaz in hypogene solutions containing carbonic acid or Ca^{++} ion may help explain the destruction of topaz at Lost River and thus give information on the alkaline-acid relations. During greisenization and metallization, a supercritical phase was involved, which was high in fluorine, but low in Ca^{++} ion. As temperatures fell, a hydrothermal phase developed that was richer in carbonic acid. The topaz, normally a very resistant mineral, formed during the initial acid stage, but broke down rapidly in the carbonic acid environment, thus hastening the argillization of the greisen, according to the equation shown below:



Silica Behavior.—The behavior of silica is noteworthy, for silica declined through greisenization and argillization. Obviously the mineralizing fluids could not have been saturated in silica, and the quartz veins seen on the surface (Fig. 2) could have received their quartz from the alteration of the wall rocks below rather than from a magmatic silica-bearing fluid. Knopf (32) suggested such an origin for the silica in the veins of the Mother Lode system in California.

Quartz veins are relatively scarce in the underground workings at Lost River. Only two veins in which the gangue is predominantly quartz were found, one on the No. 1 level that contained cassiterite, arsenopyrite, and other sulfide minerals, and one on the 365-level containing arsenopyrite, wolframite, and cassiterite plus minor other minerals. On the surface, however, quartz veinlets are relatively common, many of them being very rich in cassiterite (P. L. Killeen, personal communication). This distribution of quartz veins may reflect transition to pegmatite type of mineralization by a hydrothermal phase at some distance away from a gaseous phase which was above the critical temperature of water.

During argillization large amounts of silica were removed from greisen and granite. This gave rise to an interesting relationship in which a quartz vein containing cassiterite, wolframite and arsenopyrite that cuts greisen can be traced into moderately argillized rocks (vein A in Fig. 9). In this case, if only the section of the vein in the argillized rock were disclosed by mine workings, the quartz vein would appear to be later than the argillic alteration because of its apparent crosscutting relation. The quartz vein persisted in the argillized rock because of its quartz gangue, which could not be completely removed during argillic alteration. In considering highly argillized rocks, this writer would have reservations in assigning a post-argillic or even a contemporaneous age to quartz veinlets enclosed totally in such argillized rock. Quartz veins certainly persisted well in the argillized rock

¹ Kaolinite formula as suggested by Dr. H. S. Yoder of the Geophysical Laboratory of the Carnegie Institute.

at Lost River. Schwartz (51) shows a photograph of an argillized rock from Morenci pit, Arizona, in which quartz veins apparently cut a highly argillized rock. If this specimen had come from the Lost River mine, the quartz vein would be pre-argillic. Kerr (30) describes alteration at Santa Rita, New Mexico, in which "late" quartz veins cut highly argillized rock. The writer finds it difficult to imagine how a rock consisting essentially of solid clay presumably saturated with water at high temperature can be fractured and veined with quartz veins. If kaolinization were being effected at the same time, the solutions that were filling the quartz vein would simultaneously be abstracting silica from the wall rock being argillized. At Lost River, pervasive argillization invaded veined rock, and in two places left older quartz veins that contained ore minerals as relicts in the argillized rock.

CONCLUSIONS

1. Cassiterite at Lost River was deposited concomitantly with topaz, which indicates a temperature of deposition of at least 500° C. Ferroan sphalerite was deposited above a temperature of 425° C. These temperatures are within the range of temperatures measured at fumaroles depositing metals (9).

2. Argillic alteration, although closely related in time to ore deposition, was not directly related to ore, but rather to falling temperature. This concept is by no means new insofar as general thought is concerned, but the writer feels that it is worthwhile emphasizing the role of temperature in regulating argillic alteration associated with ore deposits. There is need for more information of actual temperature of deposition of ore with associated argillic alteration, by use of geologic thermometry, before the time relations between argillic alteration and mineralization can be stated with any degree of certainty.

3. Argillic alteration at Lost River cannot be used as a guide to the immediate proximity of ore, although it remains a useful regional criteria. Certainly widespread argillic alteration should be a very encouraging sign in this region, for it may point to a previous, higher-temperature cassiterite-depositing phase, but exploration of highly argillized areas may not necessarily outline ore.

ACKNOWLEDGMENTS

The writer is indebted to many members of the U. S. Geological Survey who contributed work incorporated in a forthcoming Geological Survey publication that led to the present paper. Most determinations of clay minerals were made by John C. Hathaway and Carol C. Parker; a few were reported and identified by the writer. J. R. Houston and G. Donald Eberlein contributed to the detailed underground mapping. The help of these workers is gratefully acknowledged here, and their individual contributions to the understanding of the mine geology will appear in the forthcoming U. S. Geological Survey report.

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H. R. Cornwall, and the writer is indebted to them for helpful suggestions. The ideas and conclusions expressed herein are the responsibility of the writer. This paper is by no means intended to be a full discussion of a very complex mine.

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