University of Nevada
Reno

Geology of the Puzzle Vein,
Creede Mining District, Colorado

A dissertation submitted in partial fulfillment of the requirements for
the degree of Doctor of Philosophy in Geology

by
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ABSTRACT

The study area is located in the Creede mining district, Mineral County, Colorado, in the central portion of the San Juan Mountains. The San Juan Mountains comprise a volcanic province consisting of a thick pile of interlayered and interfingered rhyolitic to latitic tuff and flow units. The internal structure of the volcanic province is dominated and complicated by volcano-tectonic collapse structures.

The Creede mining district is underlain by rhyolitic and quartz latitic ash flow tuffs interlayered with minor volcanic flows and lacustrine and fluvial sedimentary strata, all of Oligocene age. Intrusive rocks are subordinate and represent feeders of the volcanic units. The sub-volcanic basement under the Creede district is believed to consist of Mesozoic sedimentary beds. The structure of the district is dominated by the resurgently domed Creede caldera. Radial faults extending outward from the northwest side of the caldera define the Creede graben. The ore bodies of the district are principally fissure veins occupying the major faults which define the graben.

The mineral deposits in the Creede district have been valuable mainly for their silver content with subordinate values in lead, zinc, copper, gold and cadmium. The mineralogy of the fissure veins is predominantly quartz, barite, chlorite, galena, sphalerite, chalcopyrite, pyrite and native silver.

The ore shoots in the Puzzle vein were initially exposed by mine development during the period from 1964 to 1967 and production began in 1969. The Puzzle vein represents an unusual opportunity to study a
bonanza silver ore body as it is being exposed by mine development.

The host rock of the Puzzle vein is ash flow tuff of the Campbell Mountain Member of the Bachelor Mountain Rhyolite. The vein occupies branches of the East strand of the Bulldog Mountain fault. The vein narrows and becomes unproductive as it passes upwards into less intensely welded tuff of the upper portion of the Campbell Mountain Member of the formation.

The Puzzle vein has a maximum width of ten feet and has been exposed over strike lengths of 5,800 and 4,800 feet on the upper 9700 and lower 9360 levels of the mine respectively, although mine development has not yet reached the north end of the vein. The vein has a variable strike varying from north to N35W and dips ranging locally from 45 degrees east to vertical. The average dip of the vein changes from 67 degrees east at the south end to 57 degrees east at the north end. Mineable ore has been exposed over a vertical interval of 430 feet or a dip length of 500 feet. The vein extends for an unknown distance below the lowermost 9360 level of the mine.

The Puzzle vein is dominantly a layered barite vein formed by fissure filling. Locally pyrite and quartz are abundant. The economically valuable minerals of the ore are native silver and to a lesser extent galena. Minor amounts of rhodochrosite, fluorite, clay minerals, sphalerite, chalcopyrite and tetrahedrite are present. The paragenesis involves an early rhodochrosite-quartz-barite-galena-sphalerite suite followed in time by a chalcopyrite-pyrite-tetrahedrite suite and finally hypogene deposition of native silver.

Sulfur isotope analyses of all the common sulfur-bearing minerals
indicate that the sulfur was probably derived from at least two sources, a primordial and a crustal source. Lead isotope analyses reveal that the lead in the galena is distinctly anomalous and at least two stages of lead evolution are postulated.

The Puzzle vein is conceptually an epithermal precious metal vein. A temperature of formation of 50-200 degrees Celsius is indicated with pressure in the range of 50-150 bars. Oxidation and supergene enrichment have been minor. Trace element analyses and geologic considerations rule out a supergene origin for most of the native silver.
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Frontpiece  The Bulldog Mountain mine and mill lie in the center foreground. The Rio Grande River follows the curved outline of the Creede caldera in the background.
INTRODUCTION

The present study of the Puzzle vein was begun in April, 1968. Field work was performed during April, October and November, 1968 and October and November, 1969. A total of 3-1/2 months were spent sampling and mapping in the field. Preliminary study indicated that surface mapping and sampling by previous workers had established a geologic framework within which to study the Puzzle vein and it was decided that further geologic work on the surface would be unproductive. All field work was confined to the mine except for a brief surface reconnaissance. In this regard it should be noted that the projected outcrop of the Puzzle vein is covered with Quaternary landslide debris over most of its extent.

Geologic mapping was undertaken to determine the form, extent and structural control of the vein, to delineate the distribution of the various mineral species present in the vein in order to outline zoning patterns and to determine relative ages of the vein minerals on a macroscopic scale. Mapping of all drifts and cross-cuts was done at a scale of 40 feet to one inch and compiled at scales of 40 feet to one inch and 400 feet to one inch. Raises were not mapped because they were driven in the wallrock and are tightly lagged, affording no exposure.

Sampling was designed to cover the lateral and vertical extent of the vein as exposed and to include the entire sequence of mineral deposition for both ore and gangue minerals. In addition the wallrock was sampled to study alteration and confirm previous work regarding lithology.

Samples were subjected to laboratory study by ore microscopy, thin
section petrology, X-ray diffraction analysis, atomic absorption spectrography, mass spectrography to determine sulfur and lead isotope ratios, fire assay and electron microprobe analysis. All of the samples were collected by the writer except as noted in the section on mineralogy.

The Puzzle vein is currently being mined in the Bulldog Mountain mine by Homestake Mining Company. The ore is chiefly valuable for silver and to a lesser extent lead. Milling is done in a gravity and flotation concentrator with a nominal design capacity of 300 tons per day. Details of the mining and milling practices are given in Skilling's Mining Review (March 21, 1970, p. 1 and 8-9).
The following explanation of terms used in this paper is given for terms which are used with ambiguity in the geologic literature.

**Ore mineral** - all sulfide minerals and native metals, including minerals such as pyrite which have no economic value, which are normally studied by ore microscopy.

**Gangue mineral** - any vein mineral which is not normally studied by ore microscopy, i.e., non-opaque minerals.

**Hypogene mineral** - A mineral formed by ascending, hot fluids.

**Supergene mineral** - A mineral deposited by descending, cool fluids.

No genetic connotation is implied in the source of the fluid when the terms hypogene and supergene are used.

**Paragenesis** - This term is used in the American sense as the time sequence of mineral deposition and not in the European sense.
LOCATION AND ACCESS

The Bulldog Mountain mine is located one-half mile northwest of the town of Creede, Mineral County, Colorado. The mine is located at latitude 37 degrees 53 minutes north and longitude 106 degrees 57 minutes west in sections 23, 25 and 26 (projected), township 42 north and range 1 west, N.M.P.M. (Figure 1).

The Creede mining district includes all of the mines within a few miles of the town of Creede and consists of two legal subdivisions, the Sunnyside and King Solomon mining districts. The Puzzle vein is located in the Sunnyside district.


GEOGRAPHY

The Creede mining district is located in the central portion of the San Juan Mountains near the head of the Rio Grande River. Elevations range from 8,500 to 13,895 feet in the district. The Bulldog Mountain mine workings expose the Puzzle vein at elevations between 9,360 and 9,940 feet. The projected outcrop of the vein lies at a maximum elevation of approximately 10,800 feet.

The mountain slopes in the district are covered by grass with irregular patches of fir, pine, spruce and aspen. Timberline generally lies between 11,700 and 12,000 feet.
Figure 1 Location of the Creede mining district, Colorado with reference to the volcanic rocks of the San Juan Mountains. Modified after Steven and Ratté, 1965, p. 3.
The mining history of the Creede district began with the location of claims in 1883 and 1884 but no significant production was attained until 1891. The maximum value of production for a single year was in 1893 when ore containing a gross metal value of approximately $4,150,946 at the then prevailing prices was mined. Future production on a dollar basis may exceed the 1893 total largely as a result of new production from the Puzzle vein in the Bulldog Mountain mine. Additional details of the mining history of the Creede district are given by Emmons and Larsen (1923, p. 3) and Steven and Ratté (1965, p. 6). Total production in the Creede district to the end of 1967 has a gross metal value of approximately $70,000,000 if calculated with metal prices which prevailed at the time of production (Meeves and Darnell, 1968, p. 6 and U. S. Bureau of Mines, 1967, p. 188).

Underground exploration in the area of the Bulldog Mountain mine began with the driving of the Nickel Plate (Puzzle) adit at an elevation of 9,940 feet. The time of this initial work cannot be ascertained with certainty but it is believed to be circa 1914-1920 (A. Birdsey, 1968, oral communication). The Nickel Plate adit cut the upper portion of the Puzzle structure but it contained only a two inch wide barite vein and work was abandoned.

No further underground development was undertaken until 1961 when Bulldog Mountain, Inc. extended the Nickel Plate adit and performed underground diamond drilling (W. R. Hanscom, 1968, oral communication). The development which led to production was begun in August, 1964 by Homestake Mining Company when an adit was started at an elevation of
9,700 feet. A second adit at an elevation of 9,360 feet was begun in July, 1966 and both adits intersected substantial lengths of ore grade material. Mill construction was started in April, 1968 and completed in April, 1969; production commenced in May, 1969.

The Bulldog Mountain mine is developed by two main levels which are designated by the rail elevation of the portals at 9,360 and 9,700 feet. The 9360 and 9700 levels expose the Puzzle vein over lengths of 5,800 and 4,800 feet respectively. A drift off of the 9940 level, also called the Nickel Plate or Puzzle adit, exposes the narrow upper portion of the Puzzle vein for a length of 120 feet.

The underground development undertaken by Bulldog Mountain, Inc. and Homestake Mining Company was a direct result of a suggestion by Steven and Ratté (1960, p. 817) that the Bulldog Mountain fault zone appeared to be a favorable structure to prospect. The recognition of the exploration target in the Bulldog Mountain fault zone was a result of the U.S. Geological Survey's study of the Creede mining district.
GEOLOGY OF THE SAN JUAN MOUNTAINS

The regional geology of southwestern Colorado is discussed briefly, as it provides a framework for the ore deposits of the Creede district and because it is necessary to ascertain the nature of the subvolcanic basement in order to properly interpret isotope data from the ore bodies with reference to genesis of the ore forming fluids and their contained metals. The most comprehensive account of the geology of the San Juan Mountains is that of Larsen and Cross (1956).

The Creede mining district is located in the center of the San Juan volcanic province, an area whose physiographic expression forms the San Juan Mountains of southwestern Colorado (figure 1). The San Juan province consists mainly of volcanic rocks of Tertiary age, with a complex internal structure. The province is bordered on the north, west and southwest by metamorphic, intrusive igneous and sedimentary rocks ranging in age from Precambrian to Tertiary. Farther to the west and south are the flat lying sedimentary strata comprising the Colorado Plateau. To the east the volcanic units of the San Juan Mountains are overlapped by Quaternary valley fill of the San Luis Valley. A narrow tongue of the volcanic rocks extends southward from southwestern Colorado into northern New Mexico. The stratigraphic nomenclature used herein for the pre-volcanic rocks is that of Wilson and others (1959). Steven and Ratté (1965) has been used for nomenclature of the volcanic units in the Creede district although age assignments are based upon a later paper (Steven and others, 1967, p. D54).
STRATIGRAPHY

Along the southwestern, western and northern sides of the Tertiary volcanic pile in the San Juan Mountains the oldest rocks are intensely metamorphosed schists and gneisses of Precambrian age. Unconformably above these oldest rocks are metavolcanic rocks of the Irving Greenstone, also of Precambrian age. A sequence of moderately metamorphosed Precambrian metaconglomerate, metaquartzite and schist, termed the Needle Mountains Group, lies unconformably upon the Irving Greenstone. Unconformably above the Needle Mountains Group is the Ignacio Quartzite of Late Cambrian age. Other Paleozoic formations in ascending order are the Manitou Formation (Manitou Limestone), Harding Sandstone and Fremont Limestone of Ordovician age, the Elbert Formation, Ouray Limestone and Chaffee Formation of Devonian age, the Leadville Limestone (Leadville Dolomite) of Mississippian age, the Molas, Hermosa and Kerber Formations of Pennsylvanian age, the Maroon Formation of Pennsylvanian and Permian age, the Rico Formation of Pennsylvanian and Permian (?) age and the Cutler Formation of Permian age. There are several disconformities but no angular unconformities within the Paleozoic section.

Mesozoic strata consist of the Dolores Formation of Triassic age, the Entrada Sandstone, Wanakah Formation and Morrison Formation of Jurassic age and the Dakota Sandstone, Mancos Shale, Mesa Verde Group, Lewis Shale, Pictured Cliffs Sandstone, Fruitland Formation, Kirtland Shale and McDermott Member of the Animas Formation of Cretaceous age. In some areas the Triassic rocks are conformable with the underlying Paleozoic strata whereas in other areas this contact is marked by a disconformity and in still other areas Jurassic units lie with angular unconformity upon Precambrian or Paleozoic beds.
Cenozoic sedimentary strata include the upper portion of the Animas Formation, the Ridgeway Till and Torrejon Formation of Paleocene age, the Wasatch Formation of Eocene age and the Telluride Conglomerate and Blanco Basin Formation of questionable Oligocene age. These Cenozoic formations are conformable with the Cretaceous units in most areas north and west of the San Juan volcanic province.

To the south the Tertiary volcanic rocks of the San Juan Mountains are bordered by the Mesozoic sedimentary units typical of the Colorado Plateau. Particularly significant in the area to the south is a north trending evaporite facies in the Todilto Limestone Member of the Morrison Formation of Jurassic age. Wright (1959, p. 62) has reconstructed the depositional basin of the gypsum-anhydrite unit in the Todilto Limestone Member, and he indicates that the eastern edge of the north trending basin would cross Mineral County, Colorado in which the Creede district is located. The significance of this evaporite facies will be discussed further in the section on sulfur isotope analyses.

No volcanic rocks of Paleozoic or Mesozoic age have been noted in the San Juan Mountains although the uppermost Cretaceous beds contain gravels with clastic fragments of volcanic material (Larsen and Cross, 1956, p. 55). The main period of volcanism in this area did not begin until Eocene or early Oligocene time and it continued until the end of the Oligocene epoch (Steven, 1968, p. 113). Minor volcanic activity occurred in the Miocene epoch and possibly also in Pliocene time. The volcanic rocks in the San Juan province range in composition from basalt to rhyolite although intermediate varieties predominate. The volcanic rocks have been erupted from many centers to form a complex
interlayered pile of ash flow tuffs, tuff breccias and flows whose inter­relationship has been further complicated by considerable faulting associ­ated with the development of volcano-tectonic subsidence structures.

Recent lead and strontium isotopic studies of volcanic rocks in southern Colorado have been interpreted by Doe (1968, p. 149) with re­gard to the ultimate source of the parent magma. These isotopic results warrant discussion herein because of the temporal and spatial relation­ship of the volcanism and ore deposition in various mining districts of the region including the Creede district. Doe (1968, op. cit.) interpreted lead and strontium isotope ratios to indicate that most of the igneous rocks of the region are derived from a deep source in either the lower crust or the mantle. The isotope results rule out anatexis of Precambrian rocks as the source of the magma which produced the bulk of the silicic volcanic rocks of Cenozoic age (Doe, 1968, p. 170). A detailed discussion of the lead isotope composition of the volcanic rocks is given below in the section on lead isotopes.

The nature of the sub-volcanic basement in the central San Juan Mountains around Creede is somewhat conjectural but there is general agreement that the volcanic rocks overlie Jurassic and Cretaceous sedi­mentary units (Larsen and Cross, 1956, p. 245 and Steven and others', 1969, p. F12, F13). It is reasonable to conclude that the Creede dis­trict is underlain by carbonate beds and the Todilto evaporite unit in addition to the clastic sedimentary beds. The sedimentary carbonate units which can be projected beneath the Creede district are the Pony Express Limestone Member and the marl member of the Wanakah Formation, calcareous beds in the Todilto Limestone Member of the Morrison Forma­tion, and limestone in the Mancos Shale. The evaporite facies in the
Todilto Limestone is the only evaporite unit which can be projected beneath the Creede district.

The presence of carbonate and evaporite beds in the sub-volcanic basement of Creede is stressed because this occurrence is compatible with the lead and sulfur isotopic composition of the ore in the Puzzle vein. A postulated remobilization of lead and sulfur from the Mesozoic sedimentary units is discussed in detail in the sections on lead isotope analyses, sulfur isotope analyses and source of the ore-forming components.

STRUCTURE

The San Juan Mountains are situated on the site of a late Paleozoic and early Mesozoic positive area, the Uncompahgre-San Luis highland, and Tweto (1968, p. 569) suggests that all post-Precambrian and pre-Jurassic strata have been removed by erosion from the central portion of the range prior to the volcanism. Laramide tectonic activity domed the San Juan area and intrusive rocks of Laramide age have been identified. The doming was beveled by erosion prior to middle Tertiary volcanism and concomitant structural development. The internal structure of the San Juan volcanic province is marked by several collapse features of volcano-tectonic origin including the well-known Silverton caldera in the western part of the province. Similar features are found in the central San Juan Mountains; typical of these is the Creede caldera which is discussed in more detail in the section on the geology of the Creede mining district.
ECONOMIC GEOLOGY

The Creede district lies at or near the southwestern end of the Colorado mineral belt, depending upon the manner in which the mineral belt is defined. The Colorado mineral belt is a zone, marked by granitic intrusive bodies and mining districts, which extends from the San Juan Mountains northeastward across Colorado to a terminus in the Front Range northwest of Denver. The intrusive rocks and associated mineral deposits in the belt are of Laramide or younger age but no persistent structures of Laramide age are present. The mineral belt is the site of northeast trending Precambrian shear zones over a portion of the belt's extent. Tweto (1968, p. 571) suggests that the Colorado mineral belt is an expression of an underlying batholith which presumably rose along an ancient zone of weakness.

Many of the ore deposits of the San Juan Mountains are spatially related to granitic intrusive bodies. Other deposits appear to be directly related to local volcanism as at Summitville, Colorado (Doe, 1968, p. 171). Granitic plutons are not exposed at the surface in the vicinity of the Creede district, although they may be present at depth, and the relationship of ore deposition to volcanism is discussed below in the sections on lead isotope analyses, and the relation of ore formation to volcanism.

GEOMORPHOLOGY

It is desirable to review the late Tertiary and Quaternary history of the San Juan Mountains as this history is critical to both the reconstruction of the hypogene depositional environment of the Puzzle vein and the subsequent supergene enrichment.
Early studies of the physiography of the San Juan Mountains by Atwood and Mather (1932) resulted in the identification of a widespread erosional surface of low relief which was termed the San Juan peneplain. The proposed peneplain supposedly formed as a result of erosion which followed the major volcanic activity in Oligocene time but preceded the latest volcanism which occurred in either Miocene or Pliocene time. Following peneplain development Atwood and Mather envisaged a doming of the San Juan region.

Steven has reviewed in detail the evidence for the postulated San Juan peneplain and concluded that no peneplain cycle of erosion has occurred between the end of major volcanic activity and the present time (Steven, 1968, p. II). The evidence against the peneplain is particularly convincing in the central San Juan Mountains around the Creede district where original volcanic constructional features such as the Creede caldera and domal accumulations of lava are preserved. At least some of the geomorphic features in the vicinity of Creede such as the sediment-filled moat around the border of the resurgently domed Creede caldera probably never reached the height of the proposed peneplain (plate 1). It is concluded that the concept of deep erosion and peneplanation in the Creede area is invalid and that post-volcanic erosion has not progressed beyond canyon cutting in response to regional epeirogenic uplift and local changes in base level due to tectonic activity.

SUMMARY OF THE REGIONAL GEOLOGY

The San Juan region of southwestern Colorado is the locus of extensive middle and late Tertiary volcanism. The San Juan volcanic province is situated at the southwest end of a major regional lineament,
the Colorado mineral belt. Isotopic evidence indicates that the volcanic magma was generated at the base of the crust or in the mantle. The volcanic pile includes flows and pyroclastic units derived from numerous vents. Many of the metallic ore deposits of the San Juan region, including the Puzzle vein, are closely associated in time and space with the volcanic activity. The fault structures, which are the loci of these ore deposits, are related to stresses caused by vertical ascent and withdrawal of magma.
GEOLOGY OF THE CREEDE MINING DISTRICT

The Creede mining district has been the site of repeated geologic study. The most comprehensive and definitive studies are those of Emmons and Larsen (1923) and Steven and Ratté (1965). Unfortunately most of the bonanza silver ore in the district had been mined before systematic geologic study of the district began.

The Creede district was the site of repeated volcanic activity during the Tertiary period and the bedrock geology of the area is dominantly a volcanic pile of pyroclastic units with associated flows, intrusive feeders and sedimentary strata. Deposits of Quaternary age include debris of glacial, fluvial and landslide origin. Structural features of the Creede district are intimately related to volcanic activity and the structural pattern can be explained by vertical movements of tectonic blocks which are related to the intrusion and withdrawal of magma. The economic geology of the Creede district is closely related to the volcano-tectonic geology in both time and space.

STRATIGRAPHY

The flow and pyroclastic units of the Creede district range in composition from quartz latite to rhyolite with the earlier formations being predominantly rhyolite and the later formations being mainly quartz latite. The formations in ascending order are the Bachelor Mountain Rhyolite, Farmers Creek Rhyolite, Mammoth Mountain Rhyolite, Wason Park Rhyolite, Rat Creek Quartz Latite, Snowshoe Mountain Quartz Latite and Fisher Quartz Latite (figure 2). The youngest of the volcanic formations, the Fisher Quartz Latite, is interlayered with sandstone, shale,
Stratigraphic position of the Puzzle vein.

Figure 2 General relations of major rock units in the Creede mining district, Colorado.

Modified after Steven and Ratté, 1965, p. 12.
conglomerate and travertine of the Creede Formation. At the margins of the Creede district the formations noted above are interlayered with additional volcanic units as described by Steven and Ratté (1965, p. 13-15).

The oldest volcanic formation in the central part of the Creede district, the Bachelor Mountain Rhyolite, has been subdivided into three members, the basal Willow Creek Member, the middle Campbell Mountain Member and the uppermost Windy Gulch Member (Steven and Ratté, 1965, p. 21-26). The Puzzle vein as presently exposed is situated entirely within the Campbell Mountain Member of the Bachelor Mountain Rhyolite although the basal Willow Creek Member of this formation is also exposed in the Bulldog Mountain mine.

The total thickness of the volcanic sequence in the Creede district is not known. The base of the lowermost formation, the Bachelor Mountain Rhyolite, is not exposed in the center of the district and erosion has removed a portion of the uppermost formations, the Fisher Quartz Latite and Creede Formation. In addition the individual units in the volcanic sequence are extremely variable in thickness over short lateral distances. The Campbell Mountain Member of the Bachelor Mountain Rhyolite ranges in thickness from 0-1000 feet and the exposed portion of the underlying Willow Creek Member varies from 0-2000 feet.

The age of the volcanic rocks at Creede is considered by the writer to be well established by the age dating work of Steven and others (1967, p. 54). The oldest volcanic unit near Creede is the La Garita Quartz Latite which is partly contemporaneous with the Bachelor Mountain Rhyolite. The lower member of the La Garita Quartz Latite which underlies the Bachelor Mountain Rhyolite has been dated at 27.8 ± 1.3 million years. The Fisher Quartz Latite, the youngest volcanic formation, has
been dated at 26.4 ± 0.6 million years. The absolute ages referred to above are both potassium-argon dates of mineral separates. Details of the samples and analytical procedures are given by Steven and others (1967, p. 53). The samples for the radiometric dating did not come from the immediate area of the mines but the formations sampled can be correlated with confidence with the same formations in the vicinity of the mines (Steven, Thomas A., 1968, oral communication).

Of the volcanic formations, only the Bachelor Mountain Rhyolite, which hosts most of the ore bodies of the Creede mining district, is discussed herein. Steven and Ratte (1965, p. 11-50) give detailed descriptions of the other volcanic formations. The Bachelor Mountain Rhyolite is a tuff varying in degree of compaction from an intensely welded, fluidal rock in the basal Willow Creek Member through a densely welded eutaxitic to vitroclastic tuff in the Campbell Mountain Member to a slightly welded and noncompacted rock in the uppermost Windy Gulch Member. The continuous gradation in the degree of welding and compaction from the base to the top of the formation suggests deposition of ash flows in a single eruptive cycle.

The only major sedimentary unit in the Creede district is the Creede Formation. The distribution of the Creede Formation is of critical importance for reconstructing the land surface at the time of ore deposition as it is the youngest pre-ore formation in the immediate vicinity of the Puzzle vein. The Creede Formation consists of thin-bedded shale and sandstone with some interbedded tuff, all of lacustrine origin, sandstone and conglomerate of fluvial origin and travertine from springs. The Creede Formation has undergone an unknown amount of erosion
and the original stratigraphic thickness of the formation cannot be established. As now preserved it extends over a minimum vertical range of 2,400 feet. It was deposited in a nearly circular basin of volcanotectonic origin, the Creede caldera. The highest lacustrine deposits of the Creede Formation are now found at an elevation of 9,800 feet and the fluvial facies of the formation is exposed at a maximum elevation of 10,800 feet. The age of the Creede Formation must be the same as that of the interlayered Fisher Quartz Latite, i.e., 26.4 ± 0.6 million years.

The sub-volcanic basement is not exposed in the Creede mining district. The section on the geology of the San Juan Mountains indicated that the basement most likely consists of Jurassic and Cretaceous sedimentary formations including several carbonate horizons and an evaporite unit. Additional information on the nature of the sub-volcanic basement at Creede was provided by Steven and Friedman (1968) in a study of oxygen and carbon isotopes in travertine of the Creede Formation. The isotopic data indicated that the travertine was derived by remobilization of a sedimentary carbonate (Steven and Friedman, 1968, p. B35). The remobilization hypothesis for the travertine in the Creede Formation is consistent with a postulated remobilization of lead and sulfur as discussed below in the sections on lead isotope analyses, sulfur isotope analyses and source of the ore-forming components. It is inferred from the carbon and oxygen study of Steven and Friedman (1968, op. cit.) and from the present investigation of sulfur and lead isotopes that the volcanic magma remobilized material from the sedimentary column through which it ascended and that some of the remobilized material was deposited in the veins of the district.
Post-volcanic rocks at Creede include landslide debris, terrace gravel, fanglomerate, ground moraine, lateral moraine and terminal moraine. The post-volcanic material is post-mineralization in age.

Intrusive rocks in the Creede district consist of feeders to the volcanic units. Small volcanic necks, irregular stocks and dikes are distributed throughout the district.

STRUCTURE

The structural geology of the Creede mining district is intimately associated with the volcanic history. A major subsidence feature, the Creede caldera, occupies the southern one-half of the district. The caldera is nearly circular in outline and approximately eleven miles in diameter. Subsidence in the caldera was probably intermittent but the main subsidence that can be dated was concurrent with and followed eruption of the Snowshoe Quartz Latite (Steven and Ratté, 1965, p. 59). Following subsidence, the center of the Creede caldera was domed, presumably by the resurgent ascent of magma; doming left a topographically depressed moat at the margin of the caldera. The doming was followed by eruption of the Fisher Quartz Latite around the margin of the caldera and by deposition of the Creede Formation in the topographic moat around the resurgently domed caldera. The Rio Grande River now follows this moat as shown in the frontpiece.

Subsidence in the caldera was accompanied by down faulting along north-northwest striking normal faults which extend away from the northwest margin of the caldera. These radial normal faults define the Creede graben and are the loci of ore deposition in the district. Four of the graben faults have been the source of nearly all of the production
in the Creede district. From west to east the productive faults are
the east dipping Alpha-Corsair and Bulldog Mountain faults and the
west-dipping Amethyst and Solomon-Holy Moses faults (figure 3).

Faulting in the Creede graben was intermittent and evidence that
the latest pre-ore movement followed caldera doming is given below. The
Fisher Quartz Latite and the Creede Formation, which post-date the
development of the caldera, are offset by the faults which define the
Creede graben. The Fisher Quartz Latite was deposited, in part, on
constructional slopes of the domed portion of the caldera (Steven and
Ratté, 1965, p. 45). The Creede Formation contains clastic debris
derived from the Snowshoe Mountain Quartz Latite; the latter formation
was domed during resurgent doming of the central portion of the caldera.
Thus there is clear geologic evidence of the structural history of the
ore-bearing graben faults in relation to caldera development; the last
pre-ore faulting in the graben followed resurgent doming in the adjacent
caldera.

The Creede Formation contains minor ore mineralization at several
localities within the Creede district. The fissure veins which were
deposited in the graben faults show post-mineralization shearing and
crushing; thus structural development of the area continued, at least
on a minor scale, after ore deposition. Evidence for post-mineralization
faulting in the Puzzle vein is given in the sections on structural con-
trol of the Puzzle vein and sequence of mineral deposition.

ECONOMIC GEOLOGY

The total production of the Creede district from 1891 through 1967
has been approximately $70,000,000 if calculated as the gross metal value
Figure 3 Structural features of the Creede mining district, Colorado.
at the time of production. Silver accounts for about $40,000,000 or 57 percent of this total. Lead production follows silver in economic importance. Total lead production has been about $17,000,000 or 20 percent of the total production of the district. Zinc, gold, copper and cadmium account for the remainder of the production. The silver production was concentrated in the period from 1891 to 1930. Since 1949 lead and zinc together have exceeded silver in value each year although this pattern may change with the advent of production from the Puzzle vein in 1969.

The ore deposits of the Creede district are principally fissure veins characterized by repeated layering, cockade structure, botryoidal shapes and vugs. Some production has come from shattered masses of wallrock whose fragments are coated with ore minerals and from flat-lying disseminated bodies controlled by bedding in lacustrine sandstone of the Creede Formation.

The vein minerals noted by previous workers in the Creede district, in alphabetical order, are adularia, anglesite, ankerite, argentite, barite, calcite, cerargyrite, cerussite, chalcanthite, chalcedony, chalcopryite, chlorite, chrysocolla, chrysophase, fluorite, galena, gold, goslarite, gypsum, hematite, jarosite, kaolin, limonite, malachite, marcasite, melanterite, native silver, pyrite, pyromorphite, quartz, rhodochrosite, siderite, smithsonite, sphalerite, stephanite, stibnite and wad (Emmons and Larsen, 1923, p. 99-107, Bethke and others, 1960, p. 1336 and Steven, Thomas A., 1968, oral communication). Many of the earlier identifications were based on specimens from mine dumps and collections and on personal communication with local residents and
therefore the reliability of the identifications is somewhat questionable. No detailed statement of the relative abundances of the various minerals can be made.

The bulk of the production to date has come from the Amethyst vein and veins which branch from the Amethyst vein (figure 4). The Amethyst and related veins contain predominantly amethystine quartz, white quartz, clay, and chlorite with lesser amounts of barite, galena, sphalerite, chalcopyrite and pyrite. Native silver is the principal silver mineral in the Amethyst vein. Quartz is the most abundant gangue mineral and galena is probably the most abundant ore mineral.

Some of the Creede ores have undergone thorough oxidation subsequent to their emplacement. Galena in the Amethyst vein has oxidized to anglesite and cerussite with the former being the more abundant. Sphalerite in the Amethyst vein alters to smithsonite and goslarite although secondary zinc minerals are rare compared to the abundance of sphalerite at depth. Small quantities of malachite, chrysocolla and chalcanthite have been noted, presumably as oxidation products of chalcopyrite. Emmons and Larsen (1923, p. 124) note that no chalcocite was seen in their detailed study of the Creede ores.

The genesis of the silver minerals in the Creede district is noteworthy because of their economic importance. Native silver is the predominant silver mineral throughout the district. Acanthite and "cercargyrite" are uncommon. Steven and Ratté (1965, p. 74) note that the upper parts of the OH vein, which is a hanging wall branch of the Amethyst vein, are appreciably higher in silver content than are the lower parts. Emmons and Larsen (1923, p. 112) note that rich silver ore in...
Figure 4  Productive veins and principal mines in the Creede mining district, Colorado. Modified after Steven and Ratté, 1965, p. 4.
the Solomon-Holy Moses lode was found only near the surface and that the silver content of the ore from the Amethyst lode decreased in silver with increasing depth. Steven and Ratte (1965, p. 77) state that the high silver content in the upper parts of the oxidized ores was clearly the result of secondary enrichment. Emmons and Larsen (1923, p. 104) state that the native silver at Creede is believed to be of secondary origin. These conclusions regarding the origin of the native silver and the decrease in silver content with depth are critically reviewed in the sections on zoning and origin of the native silver in the Puzzle vein. The absence of an identifiable zone of supergene sulfide enrichment and the failure of previous workers to find chalcocite and acanthite in the ores of the Amethyst vein and elsewhere in the Creede district are puzzling in view of the common tendency of previous workers at Creede to consider the native silver to be a product of supergene enrichment. The previous studies of Creede ore deposits have also failed to identify hypogene minerals with an appreciable silver content.

There are insufficient data available to make a general statement regarding the depth of oxidation in the Creede ore bodies.

All of the major veins in the Creede district are situated in the Bachelor Mountain Rhyolite and the bulk of the production to date has come from the Willow Creek and Campbell Mountain Members of this formation. There is no obvious correlation between wallrock lithology and vein thickness or ore grade which can be used to explain the preferred association of ore and the Bachelor Mountain Rhyolite. Other formations in the district have the same lithology. The degree of welding and compaction decreases upwards in the Bachelor Mountain Rhyolite and it is likely that
the greater structural competence of the harder and more brittle lower portion of the formation resulted in more persistent and more permeable fissures towards the base of the unit. In this regard it is noteworthy that the faults of greatest displacement have been the most productive. It is concluded that the preferred association of ore with the Bachelor Mountain Rhyolite is due to structural competency and not wallrock chemistry.

The strike of the veins in the Creede district varies considerably but most veins strike between north and N40W. The veins dip from 50 to 90 degrees although dips of 60 to 80 degrees are most common. West dips predominate although the productive Alpha-Corsair and Puzzle veins dip to the east.

Both geologic and isotopic evidence of the age of the Creede ore deposits are available. The veins occupy faults which clearly cut the interlayered Fisher Quartz Latite and Creede Formation. The Fisher Quartz Latite has been dated at 26.4 ± 0.6 million years as discussed above. The Creede Formation is mineralized at various localities throughout the district. The 26.4 million year age of the Fisher Quartz Latite can be taken as the upper limit to the age of the ore bodies.

The OH vein, a branch of the Amethyst vein, contains adularia which has been dated by the potassium-argon method. The adularia belongs to the early part of the vein sequence and the dating reveals an age which corresponds to the end of the volcanic cycle in the district, i.e., about 26 million years (Bethke, P., 1968, written communication). The beginning of vein formation in the Creede district follows the cessation of volcanic activity very closely in time. There are no available data
which reveal the length of time required for deposition of the entire paragenetic sequence and there is no certainty that all of the ore minerals formed at the same time as the adularia. In addition there is no certainty that all of the veins are contemporaneous. The mineralogy of all of the major veins is similar in gross features but differs in detail and the predominance of barite in the Puzzle vein contrasts with the predominance of quartz in the other veins of the district. This contrast may simply be due, however, to the fact that only the upper part of the Puzzle vein is exposed at the present time.

The Puzzle vein is cut by an intensely altered mafic dike at a point on the 9700 level of the Bulldog Mountain mine where the vein contains only barite and amethystine quartz. The dike may have had a basaltic composition prior to alteration and if so, it may be related to the basalt of the Hinsdale Formation which has been variously dated at 12.4 ± 1.3 and 15.6 ± 0.9 million years by the potassium-argon method (Steven and others, 1967, p. D53). This reasoning is concerned with establishing a minimum age for the Creede veins and is extremely tenuous but it does not contradict the adularia dating described above and may provide a valid minimum age for the Creede veins.

SUMMARY OF THE DISTRICT GEOLOGY

The geologic history of the Creede mining district is dominated by volcanic activity during a narrow span of geologic time during the latter part of the Oligocene period. A thick pile of interlayered ash flow tuffs was erupted during an interval of approximately two million years. Structural development of the district was a direct result of the ascent and withdrawal of magma during this brief interval of volcanism. A
The dominant caldera structure is bordered by normal faults which trend radially away from the caldera. The productive fissure veins of the district were deposited in four of these radial faults which together form the Creede graben. The Puzzle vein, which is the subject of the present study, is situated in one of the four graben faults, the Bulldog Mountain fault.
STRATIGRAPHIC CONTROL OF THE PUZZLE VEIN

The host rock for the Puzzle vein is the Campbell Mountain Member of the Bachelor Mountain Rhyolite and most of the mine workings are in this unit. The 9360 level exposes the underlying Willow Creek Member of the Bachelor Mountain Rhyolite near the portal and cuts the contact between these two members (plate 2). The contact is gradational as seen in continuous exposure underground and the attitude is indefinite. The criteria used in defining the contact are described below.

The 9360 level also exposes an ancient talus near the portal. The talus consists of volcanic fragments in a partly consolidated matrix of clay and fine grained volcanic debris. This paleotalus unit is considered to be a portion of the Bachelor Mountain Rhyolite although this assignment is subjective and alternatively the unit could be assigned to one of the lateral volcanic formations which are exposed along the margins of the Bachelor Mountain Rhyolite. The paleotalus as exposed in the mine has no discernible internal structure.

The Bachelor Mountain Rhyolite has been described as an intergradational sequence of pumiceous pyroclastic rocks (Steven and Ratté, 1965, p. 21). The various members of the formation are distinguished primarily by the degree of welding and compaction. The Willow Creek Member has a fluidal texture; pumice fragments are tightly compressed and smeared into very thin layers. The overlying Campbell Mountain Member has a eutaxitic and vitroclastic texture. Pumice fragments in the Campbell Mountain Member are somewhat deformed and flattened into lenticular shapes. In the uppermost Windy Gulch Member pumice fragments are
undeformed to very slightly deformed. The degree of welding increases
downwards through the Bachelor Mountain Rhyolite and individual shards
can be distinguished in the Windy Gulch and Campbell Mountain Members
whereas it becomes increasingly more difficult to identify original
matrix fragments in the Willow Creek Member.

The contact between the Campbell Mountain and Willow Creek Members
of the Bachelor Mountain Rhyolite in the central portion of the Creede
district has been defined as a zone marked by various changes in matrix
texture, color and the abundance of lithic fragments (Steven and Ratte,
1965, p. 23). Towards the margins of the district the changes which
define the contact become less marked and Thomas A. Steven (1968, oral
communication) notes that these contact criteria are less applicable in
the Bulldog Mountain mine.

In the Bulldog Mountain mine the Willow Creek Member has a measur­
able compaction foliation whereas the Campbell Mountain Member does not
and the contact between these units is defined herein as the uppermost
exposure of measurable foliation in the Willow Creek Member although
this criterion is admittedly arbitrary.

All of the members of the Bachelor Mountain Rhyolite consist of a
microcrystalline to cryptocrystalline matrix (75-95 percent) with the
remainder being lithic fragments (5-20 percent) and phenocrysts (1-5
percent). The matrix is principally quartz with minor feldspar, mica
and clay (Steven and Ratte, 1965, p. 25). The phenocrysts are primarily
sanidine with lesser plagioclase of composition An₃₀ and minor biotite,
magnetite and ilmenite. Trace amounts of hornblende, pyroxene and quartz
are also present as phenocrysts. All of the lithic fragments are of
volcanic origin.
The Bachelor Mountain Rhyolite can best be described as a rhyolitic ash flow tuff varying from non-welded at the top to extremely welded at the base. The degree of welding is of prime importance in ore genesis because the more intensely welded rock at depth is more competent and brittle than the less intensely welded portion above. The faults which host the ore bodies do not produce the well-defined open fissures which are necessary for ore formation in the softer and less competent upper portion of the Bachelor Mountain Rhyolite. The Puzzle vein pinches and narrows upwards in the less competent portion of the formation. The tighter and less permeable faults in the upper part of the Bachelor Mountain Rhyolite may have acted as a dam to trap ore forming fluids emanating from depth. In addition, the relatively non-permeable nature of the Bulldog Mountain fault in the upper part of the formation has reduced the downward migration of meteoric water and minimized oxidation and supergene enrichment.

Wallrock alteration adjacent to the Puzzle vein is minimal. Silicification is the dominant alteration type with all gradations from quartz veining clearly cutting the wallrock to quartz veins containing numerous wallrock inclusions to silicified wallrock being present. The silicification extends only a few inches into the wallrock away from the vein except along fractures where the halo of silicification is wider. In no case is silicification seen to extend more than a few feet from the vein. The wallrock within a few inches of the vein contains traces of disseminated barite and sulfide minerals; along fractures the barite and sulfide minerals may extend a few feet into the wallrock from the main vein. The less intensely welded tuff in the upper part of the
Bulldog Mountain mine contains clay minerals but the distribution of this clay is not obviously related to proximity to the vein.

It is not possible to unequivocally state the genesis of the alteration products. The silicification and dissemination of vein minerals are most likely hypogene products. The clay in the upper part of the mine could be related to either hypogene or supergene processes in the vein or could be a deuteric feature completely unrelated to vein mineralization.

It is concluded that wallrock alteration was not a significant part of the ore-forming process in the Puzzle vein. There is no evidence that the vein-forming components have moved laterally into the fissure from the wallrock. The paucity of wallrock alteration precludes endothermic alteration as a cooling mechanism for the hydrothermal fluid or fluids.

The Bulldog Mountain Fault on the surface has an overall strike of 120°; the displacement on the surface range from 60 feet to 70 feet on the West strand and 65 feet on the East strand (Steele and Kato, 1965, p. 67). Displacement on the West strand is about 240 feet and on the East strand it is about 120 feet with the east side being dropped down relative to the west side in both cases. The aggregate effect is that about 360 feet near the southern end of the Bulldog Mountain Fault in the vicinity of the Puzzle vein.

The northern portion of the Puzzle vein occupies the East strand of the Bulldog Mountain Fault, but to the north the main part of the vein changes direction and occupies a fault which branches from the East strand (Plate 2). On the 9300 level the East strand is mineralized south of the point where the Puzzle vein leaves this fault but on the 3700 level very little vein material is present in the exposed portion of the
STRUCTURAL CONTROL OF THE PUZZLE VEIN

ATTITUDE OF THE VEIN

The Puzzle vein is situated along various branches of the Bulldog Mountain fault, a normal fault which bounds the west side of the Creede graben. On the surface the Bulldog Mountain fault can be traced and projected for a distance of 4-1/2 miles although the outcrop is covered over most of this distance by landslide debris and the total length may be even greater. Toward its south end the Bulldog Mountain fault splits and the two branches, termed the East strand and West strand, enclose a lens-shaped block of rock which is about 1500 feet wide at the surface. Farther to the south these two branches rejoin as they approach the Creede caldera (figure 3).

The Bulldog Mountain fault on the surface has an overall strike of N13W; the dips measured on the surface range from 60 NE to 70 NE on the West strand and are 65 NE on the East strand (Steven and Ratté, 1965, p. 67). Displacement on the West strand is about 240 feet and on the East strand it is about 120 feet with the east side being dropped down relative to the west side in both cases. The aggregate offset is thus about 360 feet near the southern end of the Bulldog Mountain fault in the vicinity of the Puzzle vein.

The northern portion of the Puzzle vein occupies the East strand of the Bulldog Mountain fault but to the south the main part of the vein changes direction and occupies a fault which branches from the East strand (plate 2). On the 9360 level the East strand is mineralized south of the point where the Puzzle vein leaves this fault but on the 9700 level very little vein material is present in the exposed portion of the
East strand south of the intersection with the Puzzle vein. Towards the north end of the Puzzle vein, as currently exposed, the vein splits into several branches which are designated as the A vein, E vein, G vein and I vein as shown on plate 2. The West strand of the Bulldog Mountain fault has been intersected by a cross-cut on the 9700 level but a flow of air depleted in oxygen necessitated the erection of a bulkhead and the West strand was not accessible during the present study.

Two dominant strike directions are apparent for the various branches of the Puzzle vein; these directions are north to N06W and N29W to N35W. From the southern end of the vein to its intersection with the East strand of the Bulldog Mountain fault, the Puzzle vein has an average strike of N29W. The East strand south of this intersection strikes N02W. Northward from the Puzzle-East strand intersection the Puzzle vein strikes N06W to a point where it branches into the A vein striking N01W and the E vein striking N35W. North of the A vein-E vein junction there are additional branches off the A-vein all of which follow one of the two dominant directions noted above.

The dip of the Puzzle vein varies locally from 45 NE to vertical. At the south end of the vein the average dip between the 9360 and 9940 levels is 67 NE. At the point of intersection of the Puzzle vein and the East strand of the Bulldog Mountain fault the dip between the 9360 and 9700 levels averages 64 NE. At the north end of the mine the dip between the 9360 and 9700 levels averages 57 NE. Thus there is a trend towards a slight overall flattening of the vein in a northerly direction although local variations complicate this trend.

The rake of slickensides in the plane of the vein was measured at
15 locations in the mine. The rake varies from 50 SE to 78 NW and an arithmetic mean of all the values is 84.7 degrees SE. The median value is 90 which indicates that movement on the fault is dip slip with very little if any strike slip component to the offset. At some localities slickensides of two ages were noted and slickensides are present in a few places on vein minerals. Some segments of the vein are brecciated and sheared, and contain schistose and steel galena. All of these features indicate that movement along the faults which host the vein followed at least some of the vein deposition. This conclusion is discussed further in the section of paragenesis.

Fissure veins often thicken or thin appreciably as their attitude changes and graphs were prepared to test the Puzzle vein for this feature. Graphs of vein thickness versus strike and vein thickness versus dip reveal no positive correlation between attitude and thickness, i.e., the thickness of the vein is independent of attitude. In addition there is no apparent thickening or thinning of the vein at points where the vein branches.

ANALYSIS OF MINOR FRACTURES

An analysis of minor fractures was undertaken in an attempt to elucidate the structural pattern and assist in making a stress analysis of the Puzzle vein. Equal-area stereonet plots were made of various categories of minor fractures adjacent to various segments of the vein. The minor fractures were divided into three categories; the categories are (1) fractures containing no vein minerals, (2) fractures containing gangue but no sulfide minerals and (3) fractures containing sulfide minerals with or without gangue minerals. These categories were plotted
separately for the segments of the vein with differing strikes. In this regard the vein was divided into three segments; the segments are (1) the portion south of the Puzzle-East strand intersection, (2) the portion between the Puzzle-East strand intersection and the southern junction of the A and E veins and (3) the portion north of the southern intersection of the A and E veins. It should be noted that the A and E veins may rejoin further to the north on the 9360 level but mine development has not progressed sufficiently to test this possibility on the lower level (plate 2). Separate stereonet plots were made for each category for each level. It should be noted further that most of the fractures exposed on the 9360 level are in the footwall of the vein but there should be no marked difference in attitude of similar structures in the hanging wall as the wallrock on either side of the vein is similar. A total of 355 fractures of all categories was plotted. Fractures used in this analysis have a minimum width of one inch and were selected only if they were exposed over a strike length of one-half the width of the drift or cross-cut. This selectivity was adjudged to be necessary in order to eliminate fractures caused by blasting and short fractures of irregular and poorly defined attitude. In all of the fracture analysis the pole to the plane of the fracture was plotted utilizing the lower hemisphere of the projection.

Initial plots revealed no discernible differences between the 9360 and 9700 levels in fracture orientation and no differences were detected in fractures of the various categories based upon the contained minerals. The stereonet plots did disclose a strong preferred orientation when all categories were plotted together with a shift in this
orientation with changes in the strike of the Puzzle vein. The most marked preferred orientation of minor fractures exists for the portion of the vein south of the Puzzle-East strand junction (figure 5). A maximum concentration of over ten percent of the poles per one percent of the area of the plot occurs for a plane striking north and dipping 83 degrees to the east. A second plot of poles to fractures of all categories between the Puzzle-East strand junction on the south and the southern A vein-E vein intersection on the north shows two maximum concentrations representing planes oriented N12W, 74 NE and N72W, 81 SW (figure 6). The maximum concentration of poles for the middle segment of the Puzzle vein is six percent. There is no obvious preferred orientation of minor fractures adjacent to the northern portion of the Puzzle vein. The northern portion of the vein consists of several branches of various attitudes and this diversity of major vein attitude inhibits interpretation of stress fields because a particular minor fracture cannot be related with confidence to a particular major vein.

Any structural analysis of the Puzzle vein and its subsidiary fractures must be consistent with the structural pattern and geologic history of the surrounding area. Pertinent points in this regard include the following facts. The movement on the Bulldog Mountain fault was in a normal sense. The Bulldog Mountain fault is a portion of a graben structure related spatially to the Creede caldera. The latest pre-ore faulting in the graben post-dated resurgent doming of the caldera (Steven and Ratté, 1965, p. 63). The latest pre-ore faulting in the graben also followed the latest major volcanism in the Creede district, the eruption of the Fisher Quartz Latite. The main faults which define the graben all dip between 55 and 70 degrees except locally over short
Figure 5  Orientation of poles to 191 minor fractures adjacent to the southern segment of the Puzzle vein. Contours are one, three, five, seven and nine percent of the poles per one percent of the area of the diagram.
Figure 6  Orientation of poles to 164 minor fractures adjacent to the middle segment of the Puzzle vein. Contours are one, three and five percent of the poles per one percent of the area of the diagram.
distances where both flatter and steeper dips have been noted.

The southern segment of the Puzzle vein south of the Puzzle-East strand junction is most susceptible to a simple stress interpretation. The true angle between the main vein and the pronounced maximum in minor fracture orientation is 32 degrees. It is concluded that the Puzzle vein occupies a shear direction resulting from a nearly vertical principal stress axis plunging 83 degrees in an easterly direction and a nearly horizontal axis of least stress plunging seven degrees in a westerly direction. Thus, the nearly vertical axis of principal stress lies in the plane of the minor fractures which represent a direction of least compression. The axis of least stress is adjudged to be perpendicular to the minor fractures. The intermediate stress axis would be horizontal and lie in the plane of the minor fractures. The minor fractures intersect the vein in an acute angle and represent extension fractures in the terminology of McKinstry (1948, p. 297). In this analysis it is concluded that the major veins follow shear directions.

To the north of the Puzzle-East strand intersection there is considerably less preferred orientation of minor fractures and the Puzzle vein splits into several branches of varying attitude. The complicated structural pattern for the northern and middle segments of the vein does not permit any simple interpretation of stress orientations. It is possible that the fracture pattern to the north of the Puzzle-East strand junction represents local reorientation of the stress field with time or alternatively the pattern may indicate contemporaneous interaction of local stress fields of differing orientation.

The branching pattern of the Puzzle vein in plan view north of the southern junction of the A and E veins is similar to patterns noted
elsewhere and termed cymoid loops (McKinstry, 1948, p. 315). The cymoid pattern is also seen on a larger scale in the Creede district and may be anticipated in future exploration and mine development (figure 3).

The nearly vertical axis of principal stress is consistent with a volcano-tectonic pattern of vertical forces in the Creede mining district. These vertical forces have resulted from the withdrawal and resurgence of magma and have created the caldera and graben structures which dominate the structure of the district. The Bulldog Mountain fault and its associated minor fractures are part of this larger structural environment. The Bulldog Mountain fault and the other faults which define the Creede graben are a conjugate system of shears which developed in response to the vertical volcano-tectonic forces in the area.
FORM AND EXTENT OF THE PUZZLE VEIN

The Puzzle vein has been developed over a strike length of 5,800 feet on the 9700 level and 4,800 feet on the 9360 level although these lengths do not include several branches of the vein. Some of these branches contain mineable material. Ore grade veining has been developed between elevations of approximately 9,400 and 9,830 feet or over a dip length of about 500 feet. The veining extends upwards to at least the 9940 level at the southern end of the vein although at this elevation the maximum width of the vein is two inches and no ore minerals are present.

The East strand of the Bulldog Mountain fault crops out at elevations varying from 10,560 to 10,800 feet. Detailed geologic examination and geochemical sampling have revealed no mineralization in the outcrop of the East strand of the fault (Rizzi, T. M., 1969, oral communication). Emmons and Larsen (1923, p. 186) report that samples from a 70 feet deep shaft, which is presumably located on the East strand of the Bulldog Mountain fault, assayed 87 troy ounces of silver per ton. According to Emmons and Larsen (op. cit.) the shaft was collared at an elevation of 10,800 feet. The assay data were reported verbally to Emmons and Larsen as the shaft was inaccessible at the time of their visit to the Creede district in 1911 and 1912. The shaft is still inaccessible, hence, the presence or absence of silver mineralization at the 10,800 feet elevation cannot be verified or disproven. Examination of the East strand adjacent to the shaft collar reveals a narrow fault with a width of a few inches (T. M. Rizzi, 1970, oral communication). The fault adjacent to the shaft is barren of vein mineralization. The Puzzle vein
as exposed to date appears to be a blind vein as it pinches and the grade decreases in the uppermost workings in the Bulldog Mountain mine. There is a chance, however, that some vein mineralization extends upwards to sub-outcrop under Quaternary landslide debris.

The Puzzle vein has a maximum width of ten feet. The average width is between two and three feet. Stoping began in 1969 and there are not sufficient data available to outline ore shoots and thereby determine the rake of individual ore bodies within the vein. Geologic mapping indicates that the south end of the vein is raking northwards as the dominant vein minerals barite, quartz and galena are found farther south on the 9700 level than on the 9360 level (plate 2). The same pattern is displayed by the distribution of ore shoots as they also extend farther south on the upper level than on the lower level. The northward rake of the south end of the vein is away from the Creede caldera and the hypothetical intrusive which underlies the caldera. The northward rake of the south end of the Puzzle vein is opposite to a southward rake of zoning in the vein, as discussed in detail in the section on zoning. The rake of the north end of the Puzzle vein cannot be ascertained as mining has not yet exposed the northern limit of the vein.

The texture of the vein is characterized by repeated layering parallel to the walls, curved botryoidal shapes and in places by an open central fissure (figure 7).
Figure 7  Botryoidal layering in massive pyrite in the Puzzle vein.
MINERALOGY

The mineralogy of the Puzzle vein resembles that of the older mines of the Creede district although several minerals have been identified in the present study which have not previously been reported at Creede and several minerals noted in the older mines have not been detected in the Puzzle vein.

All mineral identifications have been confirmed by X-ray diffraction analysis or electron microprobe analysis except as noted below (table 1). In cases where interpretation of X-ray patterns was uncertain, emission spectrography or electron microprobe analysis was used to verify the composition of the mineral in question. Clay mineral identifications were checked and confirmed by Mr. Keith Papke, Nevada Bureau of Mines. All minerals were identified from samples collected by the writer except as noted below in the descriptions of individual minerals. Details of the depositional sequence of the vein minerals are discussed in the section on paragenesis. The color descriptions followed by code numbers in parenthesis are based on the Munsell color system as shown in the rock color chart distributed by the Geological Society of America (1951).

DESCRIPTIONS OF INDIVIDUAL MINERALS

Acanthite (Ag$_2$S) - Electron microprobe analysis revealed the presence of acanthite in wires of native silver (figures 8 and 9). Additional silver sulfide appears to replace galena in specimens with a high content of native silver (figure 16). There is no evidence from the present study regarding the crystal habit of acanthite which could be used as a
Figure 8  Electron microprobe images showing bornite (bn) and acanthite (ac) in native silver wire (Ag); magnified 805X.
Figure 8 (continued)
Copper

Iron

Figure 8 (continued)
Figure 9  Electron microprobe images showing acanthite (ac) coating chalcocite (cc) in native silver (Ag) wire; magnified 410X.
Figure 9 (continued)
The original mineral at the time of deposition may have been either acanthite or argentite. Acanthite is definitely minor in abundance and is quantitatively very subordinate to native silver. Acanthite was not identified during field work and was seen in only six polished sections, four of which were cut from a single hand specimen.

**TABLE 1 MINERALOGY OF THE PUZZLE VEIN**

<table>
<thead>
<tr>
<th>Acanthite</th>
<th>Covellite*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumite</td>
<td>Cuprite</td>
</tr>
<tr>
<td>Barite</td>
<td>Dolomite</td>
</tr>
<tr>
<td>Bornite</td>
<td>Fluorite</td>
</tr>
<tr>
<td>Calcite**</td>
<td>Galena</td>
</tr>
<tr>
<td>Cerussite</td>
<td>Goethite</td>
</tr>
<tr>
<td>Chalcanthite</td>
<td>Goslarite</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>Hematite</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Illite</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>Copper, native</td>
<td>Mimetite</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Nontronite</td>
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<tr>
<td>Pyrite</td>
<td>Quartz</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>Silver, Native</td>
</tr>
<tr>
<td>Spalacerite</td>
<td>Tetrahedrite</td>
</tr>
<tr>
<td>Wulfenite</td>
<td></td>
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</tbody>
</table>

* Identified by ore microscopy
** Identified by other methods as noted in the text

**Alumine** \((K_2Al_6(OH))_12(SO_4)_4\) - Alumine occurs as a pale greenish yellow (10 Y 8/2) mineral with a waxy luster. It was noted only on the 9700 level and only at localities where the vein is oxidized.

**Barite** \((BaSO_4)\) - Barite is the most abundant vein mineral and is predominant throughout the vein except locally where pyrite or quartz are more abundant. Barite is intimately intergrown with galena and sphalerite and forms alternating layers with them. Tabular barite crystals as large as two inches in diameter coat vugs in the vein. Barite appears to become less abundant towards the north end of the mine, both in total amount and in relation to other minerals. Quartz, amethystine quartz and sphalerite in A132 stope on the 9360 level retain the mold of tabular...
barite crystals which have been leached and removed by hypogene fluids; there is little evidence of oxidation at this locality and barite is extremely insoluble in meteoric waters (figures 10 and 11). Hypogene leaching of barite is an important clue to the depositional environment. Barton and others (1963, p. 183) have interpreted hypogene leaching as evidence of mineralogic bottoming of an ore mineral. The leaching of barite implies bottoming of only the barite and not necessarily bottoming of the entire vein.

**Boromite** ($\text{Cu}_2\text{FeS}_4$) - Electron microprobe analysis was used to confirm the presence of boromite grains in wires of native silver (figure 8). It is not known whether the boromite is hypogene or supergene in origin. No boromite was noted in the mine during field work. Boromite was seen in only a single polished section.

**Calcite** ($\text{CaCO}_3$) - Traces of a white mineral were noted in a fracture in a single hand specimen of wallrock. The white mineral fluoresced red under ultraviolet light and was soluble in dilute hydrochloric acid. It is most likely calcite or aragonite. Calcite was not identified in the field and the identification was not confirmed by X-ray study. The paragenetic relationship of the "calcite" to the other vein minerals is not known.

**Cerussite** ($\text{PbCO}_3$) - Cerussite is the most abundant secondary lead mineral noted in the Puzzle vein. It occurs as prismatic white crystals growing in vugs in galena and as a coating on fractures. In these occurrences cerussite has been transported an unknown distance by supergene fluids to the sites of deposition. In polished sections, however, cerussite can be seen replacing galena (figure 20). A review of assay data on mill feed
Figure 10 Hand specimen of quartz showing mold of leached barite crystals

Figure 11 Hand specimen of quartz showing younger generation of small barite crystals (arrows) growing in mold of leached larger barite crystal
for the month of September, 1969, the only month for which daily data are available, shows that the average oxide lead (non-sulfide lead) content of the ore in the Puzzle vein is 2.68 percent of the total lead content. Most of this lead oxide content can be accounted for by the abundance of cerussite. Oxide lead minerals extend to the lowermost part of the vein as it is presently exposed although oxidation is generally minor.

**Chalcanthite** (CuSO$_4$·5H$_2$O) - Most of the chalcanthite in the Bulldog Mountain mine forms clusters of moderate blue (5 B 5/6) fibrous crystals on the mine walls and stalactites and stalagmites on mine timbers; thus it is post-mine in age. Depending upon ventilation conditions in the mine, mixtures of bluish copper sulfate in varying stages of dehydration are formed and it is probable that other copper sulfate minerals in addition to chalcanthite are present. One sample gave an X-ray diffraction pattern suggesting a mixture of chalcanthite and antlerite (Cu$_3$(SO$_4$)(OH)$_4$).

**Chalcedony** (SiO$_2$) - The Puzzle vein contains several varieties of silica including chalcedonic quartz or chalcedony. The chalcedony varies in color from light grey (N7) to grayish yellow green (5 GY 7/2). At several localities the chalcedony occurs as thin layers at the walls of the vein which grade outward over distances of a few inches through silicified wallrock into unaltered wallrock. At other localities the chalcedony occurs as irregular sintery and vuggy veinlets coated with sulfide minerals.

**Chalcocite** (Cu$_2$S) - A bluish grey and apparently isotropic mineral replaces galena, native silver and sphalerite as seen in polished sections.
Insufficient material is available for X-ray analysis but electron microprobe analysis reveals an approximate composition of Cu$_2$S (figure 9). The mineral phase cannot be identified with certainty and is provisionally termed "chalcocite."

**Chalcopyrite (CuFeS$_2$)** - Chalcopyrite occurs throughout the vein and is generally closely associated in space with tetrahedrite. These two minerals form layered sequences of botryoidal shapes (figure 12). Chalcopyrite also occurs as irregular grains which have grown in open spaces on the crystal faces of barite.

**Copper, native (Cu)** - Two textural types of native copper have been noted in the Puzzle vein. The first type occurs as grains and delicate arborescent crystals associated with limonitic jasper, cuprite and spangles and delicate arborescent crystals of native silver (figures 13 and 14). The first variety of native copper has been seen only in the upper part of the vein in intensely oxidized localities. The second type of native copper occurs as curved wires found in vugs in barite and other hypogene minerals. The second type of copper is nowhere abundant but is found throughout the mine. The first type of copper is adjudged to be supergene in origin. The origin of the second variety is questionable and may be hypogene or supergene or both.

**Covellite (CuS)** - Covellite was seen only in four polished sections where it occurs as irregular grains at mutual boundaries of sphalerite and galena grains, where the covellite appears to replace either the sphalerite or galena or both. Covellite is minor in abundance; it was not noted during field work.

**Cuprite (Cu$_2$O)** - Cuprite is found in intensely oxidized portions of the
Figure 12  Photomicrograph showing botryoidal intergrowth of chalcopyrite (cp) and tetrahedrite (tet); magnified 110X

Figure 13  Photomicrograph showing native copper (Cu), and cuprite (cup) coating native silver spangle (Ag); magnified 110X
Figure 14 Electron microprobe images showing native copper (Cu) and cuprite (cup) coating native silver spangle (Ag); magnified 475X.
vein on the 9700 level. It occurs as delicate nests of capillary crystals which are moderate red (5 R 4/6) in color.

Dolomite (CaMg(CO₃)₂) - Narrow veinlets of moderate orange pink (5 YR 8/4) dolomite cut across a layered barite vein at a single locality in A123 stope.

Fluorite (CaF₂) - Fluorite was identified in two samples from the 9360 level. It occurs as light greenish grey (5 GY 8/1) cubic crystals and irregular grains associated with barite and sphalerite.

Galena (PbS) - Galena is the most abundant mineral of economic importance in the Puzzle vein and it is found throughout the horizontal extent of the vein. Galena extends from the 9360 level upwards to an unknown distance above the 9700 level although it was not noted on the 9940 level. Galena is closely associated with sphalerite in both time and space. There is repeated layering of finely and coarsely crystalline varieties of galena suggesting a rhythmic change in the depositional environment and/or in the ore-forming fluid during galena deposition. A pulverulent black sooty variety of galena coats vugs in the vein and has the appearance of a supergene mineral, although a supergene origin for the sooty galena cannot be proven.

Goethite (Fe₂O₃·H₂O) - Iron oxide is present throughout the mine although minor in amount. The color of the iron oxide ranges from dark yellowish orange (10 YR 6/6) to dark yellowish brown (10 YR 4/2). Several samples have been analyzed by X-ray diffraction, revealing a high percentage of quartz in nearly every sample. Nearly pure goethite was found in only a single sample. Most of the iron oxide can best be called limonitic jasper following the terminology of Blanchard (1968, p. 9).
Goslarite \((\text{ZnSO}_4 \cdot 7\text{H}_2\text{O})\) - White capillary crystals of goslarite grow on the walls of the mine workings. Most of the goslarite noted is post-mine in age but some could be pre-mine. All of the goslarite appears to be supergene in origin.

Hematite \((\text{Fe}_2\text{O}_3)\) - Hematite occurs as a moderate reddish brown \((10\text{ R }4/6)\) coating on fractures where it is closely associated spatially with pyrite, sphalerite and galena at the northern end of the 9700 level of the mine. The hematite in the Puzzle vein may be hypogene in origin as the sulfide minerals adjacent to the hematite are unoxidized. The hematite has a greasy luster distinctly different from the earthy variety of supergene hematite found in clearly oxidized localities.

Illite - Illite was identified as the major component in a single sample taken from a three inches wide fracture in wallrock on the 9360 level of the mine. The relation of the illite to other clay minerals and the other vein minerals is not known.

Kaolinite - Kaolinite occurs as a minor constituent of clay samples which contain major illite, montmorillonite or nontronite. The kaolinite may be either hypogene or supergene in origin. It fills fractures in wallrock but does not occur as a pervasive alteration product of the wallrock.

Mimetite \((\text{Pb}_5(\text{AsO}_4)_3\text{Cl})\) - Mimetite occurs as white acicular crystals in a sample collected by Mr. T. M. Rizzi from the 9700 level of the mine. The origin is not definite but at all other localities known to the writer mimetite is considered to be a secondary mineral. The presence of mimetite is of especial interest because it is the only chlorine bearing mineral noted in the Puzzle vein.

Montmorillonite - Montmorillonite occurs as a four inches wide veinlet
filling a fracture zone on the 9360 level. The montmorillonite is veined by nontronite. The origin of the montmorillonite is uncertain. Emission spectrography revealed several percent calcium but no sodium in the montmorillonite.

Nontronite - A moderate yellow green (5 GY 7/4) waxy clay mineral has been identified as nontronite by Mr. Keith Papke, Nevada Bureau of Mines. The nontronite occurs as an irregular veinlet about 1/4 inch wide in a larger montmorillonite veinlet. The nontronite also fills vugs in the center of a barite vein. The origin of the nontronite is uncertain.

Pyrite (FeS$_2$) - Pyrite follows galena in abundance among the sulfide minerals and in places, branches of the Puzzle vein consist of massive pyrite as much as two feet thick. Pyrite is most abundant where barite is minor or absent. Pyrite occurs as botryoidal layers, with a radial structure resembling marcasite, which coat older minerals (figures 7 and 15). Typical crystal shapes are conspicuously absent in the pyrite. The texture of the pyrite resembles colloform layering but unequivocal evidence of colloidal deposition is lacking even though features believed to be characteristic of colloidal deposition such as shrinkage cracks were specifically looked for during the present study.

Quartz (SiO$_2$) - Quartz is common throughout the Puzzle vein although subordinate in amount to barite. In addition to the chalcedonic variety discussed above, quartz occurs as well developed crystals of both white quartz and amethystine quartz. In some stopes at the northern end of the 9360 level well-formed amethystine quartz gives the vein a cockscomb texture; this occurrence resembles the veins in the deeper portions of the older mines of the Creede district.
Figure 15 Photomicrograph showing botryoidal pyrite (py) coating sphalerite (sph); magnified 110X
Rhodochrosite (MnCO₃) - Rhodochrosite has been noted only on the 9360 level and it becomes abundant only at the northern end of this level as it is currently developed. The rhodochrosite forms veins several inches wide and small rhombic crystals which have grown on the faces of tabular barite crystals.

"Ruby silver" - Traces of a ruby silver mineral or minerals were noted in four polished sections where the ruby silver appears to replace the common sulfide minerals, especially tetrahedrite. There is no available evidence favoring either a supergene or a hypogene origin for the ruby silver and no evidence which rules out the presence of both supergene and hypogene varieties. Insufficient material is available for X-ray diffraction analysis and it is possible that more than one ruby silver mineral is present.

Silver, Native (Ag) - Native silver is by far the most abundant silver mineral in the Puzzle vein and it accounts for the bulk of the economic value of the ore. Distinct textural varieties of native silver are present. These textural types have different mineral associations, different tarnishing characteristics and different origins.

The first type of native silver has the form of spangles (flakes) and arborescent crystals. The first type is found only in intensely oxidized parts of the vein where it is associated with cuprite, limonitic jasper and the arborescent variety of native copper (figures 13 and 14). The first type of silver does not tarnish in situ; it is believed to be supergene in origin.

The second textural variety of native silver consists of clusters and nests of wires which fill vugs and cavities in the vein. The wire
silver variety is much more abundant than the first type. The wire silver tarnishes black in situ; it is believed to be hypogene in origin. The wire silver is found in massive veinlets of native silver as much as two inches wide and the massive veinlets are believed to represent open spaces which have completely filled with wire silver. On a freshly polished surface the massive variety of native silver has a distinctly yellowish cast.

Native silver was seen in 50 percent of the polished sections; it veins and appears to replace all of the common sulfide minerals. The wire silver variety contains numerous microscopic inclusions of the sulfide minerals whereas the spangles of silver are free of such inclusions (figures 16, 17 and 18).

**Sphalerite** (ZnS) - Sphalerite is present throughout the Puzzle vein and occurs as alternating layers with barite and galena, as individual crystals in vugs, and intermixed with galena. The sphalerite varies in color and presumably in iron content from a moderate brown (5 YR 4/4) to a moderate yellow green (5 GY 7/4). At one locality green crystals as large as 1/4 inch in diameter were found in vugs in a darker colored sphalerite veinlet. Ore microscopic study reveals a variety of textures in the sphalerite. Particularly interesting are arborescent forms of sphalerite and galena along the cleavages of barite and pelletal or framboidal shapes in sphalerite (figures 19 and 20).

**Tetrahedrite** ((CuFeZnAg)_{12}(SbAs)_{4}S_{13}) - Tetrahedrite occurs as alternating botryoidal layers with chalcopyrite, in intimate mixtures with chalcopyrite in irregular veinlets and as grains coating vugs in rhodochrosite. X-ray diffraction patterns for the grey copper mineral in the Puzzle vein
Figure 16 Photomicrograph showing acanthite (ac) and galena (gal) intergrown with native silver (Ag); magnified 110X.

Figure 17 Photomicrograph showing successive deposition of galena (gal), chalcopyrite (cp) and acanthite (ac); magnified 375X.
Figure 18  Electron microprobe images showing inclusions of galena (gal), sphalerite (sph) and acanthite (ac) in native silver wire (Ag); magnified 380X.
Figure 18 (continued)

Figure 19  Photomicrograph showing herringbone replacement by sphalerite (sph) and galena (gal) along cleavages in barite (bar); magnified 110X
Figure 20  Photomicrograph showing pelletal texture in sphalerite (sph), cerussite (cer) replaces galena (gal); magnified 110X.
are much closer to tetrahedrite reference patterns than to either tennan-
tite or freibergite patterns. Emission spectrography indicates that anti-
mony is present in greater amounts than arsenic in the tetrahedrite.

Silver is present in only trace amounts. The composition of the tetra-
hedrite was confirmed by electron microprobe analysis.

Wulfenite (PbMoO$_4$) - A single yellowish grey (5 Y 8/1) crystal of wulfen-
-ite was found in a vug in a galena-pyrite vein on the 9700 level of the
mine. The same vug contains a cerussite crystal and cerussite is wide-
spread, although not abundant, nearby. Wulfenite was not recognized any-
where else in the Bulldog Mountain mine. Wulfenite is the only molybdenum-
bearing mineral noted in the Puzzle vein.

X-ray diffraction analysis of ore samples from the Puzzle vein was
undertaken as part of a metallurgical feasibility study by the Colorado
School of Mines Research Foundation, Inc., of Golden, Colorado. The
feasibility study identified the minerals rozenite (FeSO$_4$·4H$_2$O), gypsum
(CaSO$_4$·2H$_2$O), lepidocrocite (Fe$_2$O$_3$·H$_2$O) and jarosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$)
although none of these minerals were identified during the present study

COMPARISON WITH OTHER VEINS IN THE CREEDE DISTRICT

The Puzzle vein, as exposed to date, is predominantly a barite vein.
It contains sufficient native silver to allow profitable mining. Galena
contributes to the economic value of the ore but the total sulfide con-
tent of the vein is minor relative to the barite content. The preponder-
erence of sulfate sulfur compared to sulfide sulfur has genetic signifi-
cance and this feature is discussed in detail in the sections on sulfur
isotope analyses and source of the ore-forming components. The evidence
for the postulated hypogene origin of most of the native silver is discussed in the sections on trace chemical analyses and origin of native silver.

It is unlikely that any of the veins, which have been mined to date in the Creede district, contained as high a proportion of barite as the Puzzle vein. Emmons and Larsen (1923, p. 99) note that quartz is the most abundant vein mineral. Chlorite is abundant as a vein mineral in the older mines of the district. Hematite is common in the older mines whereas it is rare in the exposed portion of the Puzzle vein.

The lead sulfate anglesite and the zinc carbonate smithsonite were not noted in the Puzzle vein although both lead carbonate and zinc sulfate are present in the Puzzle vein. Anglesite and smithsonite are common in the oxidized ores of the Amethyst vein at Creede (Emmons and Larsen, 1923, p. 104).

Several minerals, which have not previously been described in the Creede district, were identified in the present study; alunite, bornite, chalcocite, covellite, cuprite, mimetite, native copper, and wulfenite fall into this category. Several minerals noted by previous workers in other veins at Creede were not identified in the Puzzle vein; adularia, cerargyrite, chrysocolla, gold, jarosite, malachite, marcasite, melan-terite, pyromorphite, siderite, stephanite, and stibnite belong to this category.
SEQUENCE OF MINERAL DEPOSITION

The sequence of mineral deposition in the Puzzle vein, as discussed herein, involves only hypogene deposition. The various supergene minerals are seldom seen in contact with each other and cannot be placed in a reliable sequence. The supergene minerals are quite possibly contemporaneous in terms of geologic time and the only timeline that can be drawn for them is the opening of the mine. Some of the supergene minerals are at least partly post-mine in age as noted above in the section on mineralogy.

In the present study of paragenesis megascopic observation in the field and microscopic study of polished, thin and polished-thin sections were employed. The results of the megascopic and microscopic studies are in complete agreement and this agreement suggests that post-depositional changes such as sulfide remobilization have not affected the vein minerals and their relative ages.

The criteria used in determining relative ages are of critical importance in evaluating the reliability of any paragenetic study. In the present study only four criteria were used; they are (1) cross-cutting veins, (2) aligned inclusion trains, (3) prongs of one mineral penetrating another and (4) botryoidal and cockade layering. Aligned inclusion trains are simply a type of incipient veining. Prongs were used only when the length of the prong was at least twice the width of the base of the prong and only in cases where the prong extended from an otherwise straight contact. The mineral forming the prong was considered to be the younger mineral, thus prongs are also a type of incipient veining. Botryoidal layering is considered to be convex towards the younger mineral.
Bulldog Mountain mine many examples of botryoidal layering convex towards an open and unfilled fissure were seen. Botryoidal layering is concave towards the vein walls except locally where reopening of a fissure may complicate the pattern. Botryoidal and cockade layering were used as paragenetic criteria only in cases where the layers in question were of constant thickness over a length ten times as great as the thickness of the layer.

The hypogene mineral paragenesis in the Puzzle vein can be subdivided into three suites. Vein deposition began with a rhodochrosite-quartz-barite-sphalerite-galena suite followed in time by a suite consisting of chalcopyrite-tetrahedrite-pyrite and still later by deposition of wire silver. The evidence for the hypogene origin of the wire silver is given in the section on the origin of native silver. There is no evidence of temporal overlap of the three suites. There is, however, evidence of overlap in time among the minerals in any particular suite.

The Puzzle vein formed principally by fissure filling and replacement was noted only on a microscopic scale. The evidence for filling and replacement is given below. The paragenesis is considered in terms of both minerals and chemical elements (figure 21).

**RHODOCHROSITE-QUARTZ-BARITE-SPHALERITE-GALENA STAGE**

At localities in the mine where rhodochrosite is abundant, it was the first vein mineral to form. In the field, rhodochrosite coats wallrock fragments in the vein and fills fractures in the wallrock adjacent to the vein. In thin section rhodochrosite coats wallrock inclusions. At localities where rhodochrosite is abundant, quartz and barite crystals line vugs in rhodochrosite veinlets. Veinlets of quartz and barite cutting
Figure 21 Paragenesis of hypogene minerals and elements in the Puzzle vein.
veinlets of rhodochrosite are common in thin section and in underground exposures. It is concluded that the bulk of the rhodochrosite was deposited prior to deposition of quartz, barite and sulfide minerals. At a single locality at the southern end of the vein on the 9360 level rhombic crystals of rhodochrosite, approximately 1/16 inch in diameter, were found in a barite-galena vein where the rhodochrosite had grown in open spaces in tabular barite crystal faces. Thus, the time of deposition of rhodochrosite overlapped the time of deposition of barite and rhodochrosite deposition probably overlapped quartz deposition, as evidenced by the relative ages of quartz and barite as noted below. There is no available evidence that rhodochrosite was being deposited, in the exposed portion of the Puzzle vein, when sulfide deposition began.

Quartz was the first vein mineral to be deposited at localities where rhodochrosite is absent. Quartz forms the walls of the vein at several localities. There is clear evidence that quartz and barite overlapped in time of deposition. Particularly interesting examples of the relative ages of quartz and barite are shown in figures 10 and 11, which show hypogene leaching of barite. In these specimens large tabular barite crystals were coated with quartz and the barite subsequently was removed by leaching. A second generation of barite crystals grew upon the quartz and in the cavities left by removal of the earlier generation of barite. Veinlets of quartz cutting barite were noted in thin section and in the field. Crystals of white quartz, which have grown off the faces of tabular barite crystals, were noted at several localities in the mine. Similarly, barite crystals coat vugs in quartz veinlets and barite veinlets cross-cut quartz veinlets. It is likely that both amethystine and
white quartz are essentially contemporaneous. At the north end of the 9360 level well-formed crystals of both types of quartz line cavities between barite crystals; the amethystine and white quartz crystals in this part of the mine are of equal size. At localities showing the relative ages of quartz and barite, barite is the younger mineral at 55 percent of the localities. Thus it is inferred that barite deposition continued after quartz deposition ceased. Additional evidence on the relative ages of barite and quartz is provided by the relationships of quartz versus sphalerite-galena and barite versus sphalerite-galena.

Barite is older than sphalerite in 62 percent of the cases where their mutual boundary allows determination of relative ages. Barite is earlier than galena in 61 percent of the occurrences which permit the establishment of age relationships. From the quantitative data concerning quartz versus barite and barite versus sphalerite-galena, it is inferred that quartz deposition preceded the initial sphalerite and galena deposition and that sphalerite and galena deposition continued after quartz deposition ceased. Quartz was seen in definite mutual boundary relationships with sphalerite and galena at only 22 localities; because of the small number of occurrences of quartz versus sphalerite and galena the relative ages are less certain than in the case of barite versus sphalerite and galena. The quartz is later than the sphalerite and galena in 13 of the 22 cases but the relationships of quartz to barite and barite to galena-sphalerite suggest that the quartz is predominantly earlier than the sphalerite and galena. In any case the depositional periods of quartz, barite, sphalerite and galena overlap.

At many localities in the Puzzle vein barite is interlayered with sphalerite and/or galena. The sphalerite in these occurrences has a
botryoidal texture and the sphalerite has grown on the earlier barite. Later barite has nucleated and grown on the convex surface of the sphalerite. Similarly galena crystals are found between barite layers; the galena crystals have grown on the faces of earlier barite crystals and later barite has formed layers coating the galena. Sphalerite and galena are intimately intergrown on a microscopic scale and grains of each mineral are riddled with inclusions of the other mineral. Sphalerite is earlier than galena in 61 percent of the cases where their mutual boundary relationships are definitive regarding relative ages. It is concluded that sphalerite and galena are largely contemporary, with galena deposition at some localities continuing after sphalerite deposition ceased.

The rhodochrosite-quartz-barite-sphalerite-galena suite form the bulk of the Puzzle vein and all subsequent hypogene minerals are quantitatively minor. The deposition of the rhodochrosite-quartz-barite-sphalerite-galena suite was followed by minor faulting along the Puzzle vein. Some of the galena has curved cleavages and slickensided galena was noted. Some of the barite in the vein shows crushing and fragments of layered barite have been contorted, fractured and brecciated. Rhodochrosite and quartz both exhibit undulatory extinction in thin section.

CHALCOPYRITE-TETRAHEDRITE-PYRITE STAGE

The deposition of the rhodochrosite-quartz-barite-sphalerite-galena suite was separated from the younger chalcopyrite-tetrahedrite-pyrite stage by a period of minor faulting. There is no available evidence that the minerals of the chalcopyrite-tetrahedrite-pyrite stage have been affected by the minor faulting.
Chalcopyrite and tetrahedrite clearly had overlapping periods of deposition. Numerous examples of interlayered chalcopyrite and tetrahedrite were seen in polished sections (figure 12). Chalcopyrite and tetrahedrite form segmented veinlets in earlier minerals (figure 21). In 68 percent of the cases where textural relationships allowed determination of age relationships, chalcopyrite is older than tetrahedrite. Therefore it is inferred that chalcopyrite deposition preceded tetrahedrite deposition at some localities and that tetrahedrite continued to form after chalcopyrite deposition ceased. The relative ages of tetrahedrite and chalcopyrite were determined during field work at a single locality at the intersection of the East strand fault with the Puzzle vein on the 9360 level; at this point the sequence of layering from the walls inward is barite, galena, chalcopyrite and finally tetrahedrite adjacent to a central fissure.

Pyrite is most abundant where chalcopyrite is rare and tetrahedrite is rare or absent; pyrite is minor where chalcopyrite and tetrahedrite are most abundant. For these reasons the relative ages of pyrite versus chalcopyrite and tetrahedrite are not well known although the available evidence indicates that pyrite, chalcopyrite and tetrahedrite all had overlapping periods of deposition. In addition pyrite is clearly later than quartz, barite, sphalerite and galena. At the north end of the 9700 level pyrite is the predominant vein mineral, and it forms the curved surfaces of deposition adjacent to an unfilled central fissure.

NATIVE SILVER STAGE

The last hypogene mineral to form in the Puzzle vein was native silver. The evidence for the hypogene origin of some of the native silver
is given below in the sections on trace analysis, zoning and the origin of native silver. The native silver of hypogene origin occurs as wires occupying vugs and veinlets in all of the older minerals. The native silver is devoid of detectable copper, lead, zinc, antimony, arsenic, and iron. The purity of the native silver suggests that the ore fluid was depleted in these elements during silver deposition as native silver from other deposits often contains appreciable amounts of these elements. The tetrahedrite contains only a trace of silver, indicating that the ore fluid may have been depleted in silver at the time of tetrahedrite deposition. Tetrahedrite from argentiferous mineral deposits often contains appreciable silver. The paucity of silver sulfosalt minerals in the Puzzle vein also suggests that the silver content of the ore fluid may have been low during the stages of base metal deposition. It is concluded on these bases that the native silver deposition was separated in time from the chalcopyrite-tetrahedrite-pyrite suite. There is no available quantitative measure of the duration of this time separation of the silver and the earlier sulfide minerals.

SUMMARY OF THE SEQUENCE OF MINERAL DEPOSITION

The trace amounts of ruby silver, acanthite, bornite, covellite, chalcocite, fluorite, dolomite, hematite and some of the native copper cannot reliably be assigned either hypogene or supergene origins and therefore cannot be integrated into the paragenetic sequence.

The chemical paragenesis as shown in figure 22 involves a sequence of major cation deposition beginning with manganese and continuing with barium, zinc, lead, copper-iron-antimony and ending with silver. Cadmium is found in the sphalerite and arsenic is present in the tetrahedrite.
In general oxygen-bearing species were deposited early and sulfur-bearing species formed late although there was considerable overlap of oxygen and sulfur as evidenced by the partial contemporaneity of rhodochrosite, quartz and barite, by barite itself, and by the overlap of barite and sphalerite and galena. The paragenesis consists of a sequence from early to late of carbonate, silicate, sulfate, sulfide and native metal.

The mineralogical sequence of deposition involved three separate mineral suites with no individual mineral being found in more than one suite. The spatial overlap of the three suites suggests that either the depositional environment or the composition of the ore-forming fluid may have been changing with time during the vein formation.

FISSURE FILLING VERSUS REPLACEMENT

The main textural features of the Puzzle vein such as botryoidal layering and cockade texture can be explained by filling of an open fissure. The fissure which contains the Puzzle vein remains open today in the center of the vein, for widths of several inches to as much as one foot. The vein is very porous and vuggy and crystals of barite, quartz, sphalerite and galena, terminating in open cavities are widespread. It is unlikely that the porous nature of the Puzzle vein could have developed via replacement.

There are few reliable criteria of replacement which have been noted in the present study. The development of galena and sphalerite along the cleavage planes of barite (figure 19) and the distribution of acanthite in galena (figure 16) are adjudged to be replacement phenomena; with the galena and sphalerite replacing the barite in the former example and the acanthite replacing the galena in the latter case. The formation of
irregular grains of tetrahedrite across a segmented veinlet of tetrahedrite and chalcopyrite in galena is evidence that the irregular tetrahedrite grains have replaced the galena (figure 22). The occurrence of acanthite in the center of a galena grain may be evidence of replacement of the galena by acanthite as the galena is also rimmed with chalcopyrite, acanthite and pyrite (figure 17). The development of cerussite around galena is considered to be evidence that the cerussite has replaced the galena (figure 20). No other unequivocal evidence of replacement was noted.
Figure 22  Photomicrograph showing tetrahedrite (tet) which has replaced galena (gal); magnified 110X.
COMPOSITION OF THE VEIN

The mineralogical composition of the Puzzle vein has been reviewed above but a more detailed description of the chemical composition of the vein is needed. An analysis of the mill concentrate is presented below as a qualitative statement of the composition of the vein (table 2).

**TABLE 2 EMISSION SPECTROGRAPHIC ANALYSIS OF MILL CONCENTRATE**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>2,000</td>
<td>Mn</td>
<td>2,000</td>
</tr>
<tr>
<td>As</td>
<td>700</td>
<td>Mo</td>
<td>200</td>
</tr>
<tr>
<td>Au</td>
<td>N</td>
<td>Nb</td>
<td>N</td>
</tr>
<tr>
<td>B</td>
<td>N</td>
<td>Ni</td>
<td>10</td>
</tr>
<tr>
<td>Ba</td>
<td>5,000</td>
<td>Sb</td>
<td>3,000</td>
</tr>
<tr>
<td>Be</td>
<td>1</td>
<td>Sc</td>
<td>5</td>
</tr>
<tr>
<td>Bi</td>
<td>N</td>
<td>Sn</td>
<td>N</td>
</tr>
<tr>
<td>Ca</td>
<td>1,000</td>
<td>Sr</td>
<td>700</td>
</tr>
<tr>
<td>Cd</td>
<td>1,000</td>
<td>Ti</td>
<td>500</td>
</tr>
<tr>
<td>Co</td>
<td>15</td>
<td>V</td>
<td>10</td>
</tr>
<tr>
<td>Cr</td>
<td>N</td>
<td>W</td>
<td>N</td>
</tr>
<tr>
<td>Cu</td>
<td>7,000</td>
<td>Y</td>
<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>15,000</td>
<td>Zn</td>
<td>10,000</td>
</tr>
<tr>
<td>La</td>
<td>20</td>
<td>Zr</td>
<td>30</td>
</tr>
<tr>
<td>Mg</td>
<td>200</td>
<td>N</td>
<td>not detected</td>
</tr>
</tbody>
</table>

N - not detected

The silver is present principally as native silver with very minor acanthite and one or more ruby silver minerals. The silver content of the various sulfide minerals is discussed in the following section on trace analyses. Arsenic and antimony are present as tetrahedrite although minor arsenic is found in mimetite and as a trace constituent of pyrite. Barium and probably strontium are found as barite. Calcium is present in the rhodochrosite, dolomite and clay minerals. Cadmium is present in sphalerite. Emission spectrographic analyses of sphalerite reveal a cadmium content in the range of 100 to 10,000 parts per million (ppm). Cobalt
and nickel were not detected in any of the spectrographic analyses of the common vein minerals although minor amounts of each are present in the mill concentrate. Cobalt and nickel may have been added during milling and may not be present in the vein. Copper is found in trace amounts in all of the hypogene sulfides in addition to the substantial amount present in the copper minerals. Iron is found mainly in pyrite, chalcopyrite, sphalerite and goethite. Lanthanum was not detected in spectrographic analyses of the various hypogene minerals. Magnesium is found as dolomite. Manganese is present as rhodochrosite. The only molybdenum mineral detected during the present investigation is wulfenite. The source of the titanium and zirconium is not known. They may have been introduced during milling or may be contributed by fragments of wallrock in the ore.

It is difficult to make reliable quantitative statements regarding elemental abundances in the vein. The exposed portion of the vein may not be representative of the overall extent of the vein as there is evidence of zoning within the vein. The Puzzle vein has undergone a limited amount of oxidation. Leaching by supergene fluids may have transferred material from the wallrock into the vein and removed material from the vein. Wallrock included in the ore probably accounts for some of the elements noted in table 2 and lanthanum, titanium and zirconium may fall into this category. The results of chemical analyses of four samples of the Willow Creek Rhyolite from the Creede district are given by Larsen and Cross (1956, table 21). All of these analyses revealed TiO₂ ranging from 0.15 to 0.19 weight percent. It is likely that the titanium content of the Campbell Mountain Rhyolite, which hosts the Puzzle vein and overlies
the Willow Creek Rhyolite, is of the same order of magnitude; both volcanic units are part of a single eruptive unit. It seems reasonable to conclude that some of the titanium detected in the mill concentrate is contributed by wallrock fragments in the ore.

The four analyses of Willow Creek Rhyolite described above did not reveal any detectable ZrO$_2$ but analyses of rhyolite from other localities in the San Juan province indicates that ZrO$_2$ is present in amounts ranging from 0.03 to 0.04 weight percent (Larsen and Cross, 1956, p. 167). Again it seems reasonable to infer that the wallrock in the ore is the source of at least some of the zirconium noted above in Table 2.
The hypogene minerals in the Puzzle vein were sampled and separated with a view to analyze each for trace elements insofar as the trace element content might pertain to genesis. The minerals treated in this fashion were barite, galena, sphalerite, chalcopyrite, tetrahedrite, pyrite and native silver. Analyses of the mineral separates were performed by atomic absorption spectrography, emission spectrography, fire assay and electron microprobe analysis. Instrument parameters and analytical techniques for the various methods are described in appendices A, B and C. Splits of the samples used for trace analyses were used for lead and sulfur isotope analyses. Polished grain mounts and X-ray diffraction analyses were used to check the purity of the separated samples. The galena samples contained minor sphalerite contamination and the sphalerite samples contained minor galena contamination due to the extremely fine-grained nature of their intergrowths. This contamination is not sufficient to affect the results and conclusions presented herein.

SILVER ANALYSES

The distribution of silver in the Puzzle vein is of critical importance for various reasons. The silver is of dominant economic importance in the vein as well as in numerous similar deposits in southwestern Colorado and elsewhere. The distribution of silver can be expected to reflect both hypogene and supergene processes in the vein. In an effort to elucidate the distribution of silver in the Puzzle vein and to better understand the genesis of the native silver, all of the hypogene sulfide minerals were analyzed for silver by atomic absorption spectrography.
The results of the atomic absorption analyses are given in Table 3 and details of the method are given in Appendix A.

**TABLE 3 SILVER CONTENT OF SULFIDE MINERALS**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineral</th>
<th>Silver (ppm)</th>
<th>Silver (troy oz./ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.22</td>
<td>Galena</td>
<td>450</td>
<td>13.13</td>
</tr>
<tr>
<td>50.22</td>
<td>Galena</td>
<td>250</td>
<td>7.29</td>
</tr>
<tr>
<td>84.221</td>
<td>Galena</td>
<td>430</td>
<td>12.54</td>
</tr>
<tr>
<td>84.222</td>
<td>Galena</td>
<td>935</td>
<td>27.27</td>
</tr>
<tr>
<td>86.22</td>
<td>Galena</td>
<td>990</td>
<td>28.88</td>
</tr>
<tr>
<td>43.26</td>
<td>Sphalerite</td>
<td>&lt;100</td>
<td>&lt;2.91</td>
</tr>
<tr>
<td>44.26</td>
<td>Sphalerite</td>
<td>&lt;100</td>
<td>&lt;2.91</td>
</tr>
<tr>
<td>1.23</td>
<td>Pyrite</td>
<td>95</td>
<td>2.77</td>
</tr>
<tr>
<td>47.23</td>
<td>Pyrite</td>
<td>3.2</td>
<td>0.09</td>
</tr>
<tr>
<td>61.23</td>
<td>Pyrite</td>
<td>16.5</td>
<td>0.48</td>
</tr>
<tr>
<td>84.24</td>
<td>Tetrahedrite</td>
<td>44</td>
<td>1.28</td>
</tr>
<tr>
<td>84.25</td>
<td>Chalcopyrite</td>
<td>100</td>
<td>2.92</td>
</tr>
<tr>
<td>86.25</td>
<td>Chalcopyrite</td>
<td>23</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Galena contains the most silver of the minerals analyzed with five samples ranging from 250 to 990 ppm; the arithmetic mean of the five galena samples is 611 ppm. The sphalerite samples contain less than 100 ppm. No exact figures can be given for the sphalerite because of the presence of galena in the samples. Two chalcopyrite samples have a mean silver content of 61.5 ppm and three pyrite samples have a mean of 38.2 ppm silver. The single tetrahedrite sample contained only 44 ppm silver, a surprisingly low value for tetrahedrite in an argentiferous deposit.

The low but quite variable silver content in the various sulfide minerals suggests that at least some of the silver is contained in discrete but submicroscopic silver minerals. The galena contains considerably more silver than any of the other sulfide minerals and the distribution
of silver in galena was examined in more detail by electron microprobe analysis. Appendix B given instrument parameters for the microprobe. The electron microprobe examination of galena revealed no detectable silver which could be contained in the galena lattice. Figure 23 shows several galena grains to be devoid of detectable silver and a single galena grain which contains traces of silver due to discrete particles of acanthite. The detection limit for silver in this microprobe analysis of galena is 200 ppm.

The silver content of the tetrahedrite was also checked during the microprobe study. Both the microprobe investigation and emission spectrographic analysis of the tetrahedrite revealed a real but low silver content, thus confirming the atomic absorption data listed in Table 3.

ANALYSIS OF NATIVE SILVER

The Puzzle vein contains distinct textural varieties of native silver and their occurrence and characteristics are reviewed as background for a discussion of trace analysis results. The more abundant variety of native silver consists of wires which tarnish black and contain numerous inclusions of all of the common hypogene sulfide minerals. The less abundant variety consists of flakes or spangles of silver which do not tarnish and are free of sulfide mineral inclusions. The wire silver is found throughout the mine in spatial association with the hypogene base metal sulfide minerals whereas the spangles of silver are found only in intensely oxidized localities. In an effort to chemically distinguish these varieties of silver; detailed emission spectrography, fire assay and electron microprobe analysis were undertaken.

The emission spectrographic results revealed no significant differences
Figure 23  Electron microprobe images showing the distribution of silver in galena (gal); magnified 400X. The traces of silver in the large grain at the right are due to discrete grains of acanthite.
in trace element contents of the two textural varieties of native silver. The wire silver contained 800 ppm iron, 300 ppm copper, 800 ppm zinc and 100 ppm lead; all of these elements can be attributed to inclusions of chalcopyrite, pyrite, sphalerite and galena in the wire silver (figure 18). The spangles of silver contained 200 ppm copper which can be attributed to attached grains of cuprite and/or native copper (figure 13). The spectrographic examination revealed that both varieties of native silver contained mercury.

Electron microprobe analysis was employed to test the two varieties of native silver for contained trace elements in such a manner that contamination from grains of other minerals could be avoided. The microprobe analysis revealed no detectable antimony, arsenic, copper, gold, lead, selenium, tellurium or zinc in either variety of native silver. Detection limits for the various elements were in the range of 100 to 1000 ppm. The microprobe analyses revealed the presence of mercury in both varieties of native silver, although it was not possible to measure the mercury content of the silver with the microprobe.

Seven samples of native silver including both the wire silver and the spangles were analyzed for gold by fire assay in an effort to further evaluate the trace element content of the silver with a method for gold having a lower detection limit than either the emission spectrography or the electron microprobe analysis. It was felt by the writer that gold would be one of the most likely trace elements in the native silver. The detection limit for gold by fire assay is 0.005 troy ounces per ton which is equivalent to 0.1714 ppm. The samples analyzed for gold by fire assay included a sample weighing 62.40 grams in an effort to minimize the detection limit and cupellation loss. All of the fire assays were umpire
quality and involved duplicate analyses. None of the samples subjected
to fire assay contained detectable gold.

All of the native silver from the Puzzle vein is remarkably pure
and free of detectable trace elements other than mercury. Both the
wires and spangles contain mercury.

MERCURY ANALYSES OF MINERAL SEPARATES

The two textural varieties of native silver and the various hypogene
minerals were analyzed for mercury. Details of the mercury analytical
procedure, which involved the use of a Lemaire Instruments Company de-
tector, are given in Appendix C. The results of the analyses are given
in Table 4.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineral</th>
<th>Mercury (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.22</td>
<td>Galena</td>
<td>&gt;75.2</td>
</tr>
<tr>
<td>50.22</td>
<td>Galena</td>
<td>0.75</td>
</tr>
<tr>
<td>43.26</td>
<td>Sphalerite</td>
<td>7.90</td>
</tr>
<tr>
<td>44.26</td>
<td>Sphalerite</td>
<td>3.01</td>
</tr>
<tr>
<td>1.23</td>
<td>Pyrite</td>
<td>7.52</td>
</tr>
<tr>
<td>47.23</td>
<td>Pyrite</td>
<td>21.0</td>
</tr>
<tr>
<td>61.23</td>
<td>Pyrite</td>
<td>not detected</td>
</tr>
<tr>
<td>84.24</td>
<td>Tetrahedrite</td>
<td>20.7</td>
</tr>
<tr>
<td>86.25</td>
<td>Chalcopyrite</td>
<td>7.52</td>
</tr>
<tr>
<td>52</td>
<td>Silver, spangles</td>
<td>&gt;75.2</td>
</tr>
<tr>
<td>127.1</td>
<td>Silver, wires</td>
<td>&gt;75.2</td>
</tr>
<tr>
<td>127.2</td>
<td>Silver, wires</td>
<td>19.9</td>
</tr>
<tr>
<td>128.4</td>
<td>Silver, wires</td>
<td>not detected</td>
</tr>
<tr>
<td>149.1</td>
<td>Silver, wires</td>
<td>35.0</td>
</tr>
<tr>
<td>149.2</td>
<td>Silver, wires</td>
<td>&gt;75.2</td>
</tr>
<tr>
<td>26.211</td>
<td>Barite</td>
<td>1.39</td>
</tr>
<tr>
<td>26.212</td>
<td>Barite</td>
<td>1.65</td>
</tr>
<tr>
<td>30.21</td>
<td>Barite</td>
<td>1.39</td>
</tr>
</tbody>
</table>
The mercury content of the native silver and the sulfide minerals galena, sphalerite and pyrite is extremely variable. The barite has a much more uniform mercury content. Samples of mill concentrate, which contains appreciable amounts of both the sulfide minerals and native silver, also have a rather uniform mercury content ranging from 30.8 to 67.7 ppm and with a mean for five samples at 45.9 ppm. The variable mercury content of the individual minerals is adjudged to be due to an inhomogeneous distribution of trace quantities of mercury. The inhomogeneity of mercury distribution in individual minerals is enhanced due to the small sample size used in the analyses. No mercury minerals were identified in the present study.

COMPARISONS WITH OTHER MINING DISTRICTS

All of the minerals from the Puzzle vein which were analyzed for trace elements by the various methods noted above, are remarkably pure and free of trace elements. Particularly noteworthy in this regard are the galena and native silver, the minerals of dominant economic importance in the deposit. In this section the trace element contents of the galena and native silver from the Puzzle vein are compared to trace element contents of these minerals from other districts. In the next section the trace element content of the Puzzle vein galena is compared to the results of laboratory syntheses of galena.

Boyle (1968, p. 33) states that galena samples from various localities throughout the world vary in silver content from less than one ppm to 8,000 ppm. The Puzzle vein galena, which has a silver content of less than 200 ppm, is surprisingly low in silver in view of the argentiferous nature of the deposit. A crystal of galena from the Coeur d'Alene district
of Idaho contained 1,200 ppm silver (Fryklund, 1964, p. 10). Silver in fifteen galena samples from the Keno Hill district in the Yukon Territory of Canada ranges from 1,650 to 6,300 ppm (Boyle, 1965, p. 270). The low silver content of the galena from the Puzzle vein, compared to galena from ores of the other argentiferous districts, suggests that either the ore-forming fluid which deposited the Puzzle vein was depleted in silver at the time of galena deposition or that the environment of deposition inhibited incorporation of silver into the galena as it formed.

The purity of the native silver in the Puzzle vein contrasts markedly with published analyses of native silver of undoubted hypogene origin from several Canadian localities such as Cobalt, Gowganda, and Silver Islet in Ontario and the Eldorado mine at Great Bear Lake in the Northwest Territories. At all of these localities native silver contains appreciable antimony, nickel and mercury (Boyle, 1968, p. 18). Spectrographic analyses reveal that the antimony content of native silver from the Cobalt district is in the range of 1-10 percent (Boyle, op. cit.). Native silver from Gowganda and Great Bear Lake contains antimony in the ranges of 0.1 - 1.0 percent and 0.01 - 0.1 percent respectively. Nickel in native silver from Great Bear Lake and Cobalt is in the range of 0.1 - 1.0 percent. Native silver from Gowganda contains 0.01 - 0.1 percent nickel. Native silver from Silver Islet, Cobalt and Gowganda contains 0.1 - 1.0 percent mercury. Native silver from Great Bear Lake contains 0.01 - 0.1 percent mercury. It should be noted that all of these Canadian occurrences are located in Precambrian terranes and are associated with mineral assemblages such as nickel and cobalt arsenide and sulfide minerals which are generally considered to represent a higher
temperature assemblage than the Puzzle vein. Lindgren (1933, p. 603-610) classifies these Canadian deposits of native silver as mesothermal in origin.

Other classic localities at which the native silver is considered to be hypogene in origin are Kongsberg, Norway, and Andreasberg, Germany. The Kongsberg deposits are veins in Precambrian metamorphic rocks and the Andreasberg ores are veins in Silurian slates and quartzite. Both of these European districts are marked by the presence of nickel and cobalt arsenide and sulfide minerals so common in deposits of the Cobalt type. Published analyses of the Kongsberg native silver reveal appreciable antimony, gold and mercury in the silver (Palache and others, 1955, p. 97). The Kongsberg native silver contains 0.581 percent antimony, 1.130 percent mercury and 0.004 percent gold (Palache and others, op. cit.). Lindgren (1933, p. 600) considers the Kongsberg and Andreasberg veins to be mesothermal in origin.

The mercury in the native silver is particularly interesting in that previous workers have drawn genetic conclusions from the mercury content of silver. Boyle (1968, p. 17) states that mercurian silver is mostly of hypogene origin and that silver of supergene origin rarely contains mercury. Sample number 52, which has a mercury content greater than the 75.2 ppm upper limit of the instrument, is believed to be of supergene origin. Samples 127.1, 127.2, 128.4, 149.1 and 149.2 are all wire silver which is believed to be of hypogene origin. The wire silver samples contain mercury ranging from not detected to greater than 75.2 ppm. It is apparent that the two textural varieties of native silver in the Puzzle vein cannot be distinguished by their mercury content. The mercury
content of silver in the Puzzle vein is low compared to deposits such as at Cobalt and Gowganda in Ontario where native silver of hypogene origin contains as much as 1000 - 10,000 ppm mercury (Boyle, 1968, p. 18).

There appears to be a general lack of recognition of native silver deposits of hypogene origin in geologic terranes of Cenozoic age. The higher trace element content of the older and higher temperature Cobalt type of native silver deposit seems logical from the standpoint of crystal chemistry. It seems equally logical that hypogene native silver formed at considerably lower temperatures, such as the Puzzle vein, would have a lower trace element content. Data presented below in the section on the environment of hypogene deposition indicate that the exposed part of the Puzzle vein was deposited under epithermal conditions. The temperature in the Puzzle vein may have been at the lower end of the epithermal range during native silver deposition. The native silver in the Puzzle vein formed late in the paragenetic sequence and the ore fluid may have been depleted in elements such as antimony which are normally found in native silver. The low silver content of the tetrahedrite from the Puzzle vein was discussed in the section on paragenesis and given as evidence that tetrahedrite and native silver deposition were separated in time. It is concluded that the absence of an appreciable trace element content in the wire silver of the Puzzle vein does not rule out a hypogene origin. The genesis of the wire silver is discussed in detail in the section on the origin of native silver.

COMPARISON WITH SYNTHETIC SYSTEMS

Numerous laboratory studies of the system PbS-Ag₂S have been made and the results indicate a marked increase in the silver content of
galena with increasing temperature. These studies also show an increase in the silver content of galena as the bismuth content increases. The galena from the Puzzle vein contains no detectable bismuth. The solubility of \( \text{Ag}_2\text{S} \) in galena was studied by Van Hook (1960, p. 769) who determined that the solubility is 0.4 mol percent at a temperature of 700 degrees Celsius. Hutta and Wright (1964, p. 1012) studied this solubility over the range of 300–600 degrees Celsius and found an increasing solubility with increasing temperature ranging from 0.03 mol percent at 300 degrees Celsius to 0.6 mol percent at 600 degrees Celsius. Ramdohr (1960, p. 594) suggests that the probable solubility limit of \( \text{Ag}_2\text{S} \) in galena is in the range of 0.1 to 0.01 mol percent. The galena from the Puzzle vein contains less than 200 ppm silver which is equivalent to a maximum of 0.02 weight percent of Ag or 0.02295 weight percent of \( \text{Ag}_2\text{S} \). Converting the 0.02295 weight percent of Ag to \( \text{Ag}_2\text{S} \) gives approximately 0.023 mol percent \( \text{Ag}_2\text{S} \), the maximum \( \text{Ag}_2\text{S} \) content of the Puzzle vein galena. Thus it can be seen that the \( \text{Ag}_2\text{S} \) content of the galena from the Puzzle vein is consistent with the range of solubility suggested by Ramdohr (op. cit.). In this discussion it should be noted that the \( \text{Ag}_2\text{S} \) content of galena refers to the solubility of the \( \text{Ag}_2\text{S} \) molecule in the galena lattice and not to admixed grains of acanthite. The Puzzle vein galena cannot properly be termed argentiferous.

ZONING OF TRACE ELEMENTS

The widespread and abundant minerals barite and galena were analyzed by emission spectrography to test for the presence of trace elements which might aid in delineating zoning within the Puzzle vein. No other minerals are sufficiently widespread to be useful for studying zoning of
trace elements. Nine barite samples were selected from localities which represented the full vertical and horizontal extent of the vein including the 9940 level. The emission spectrography analyses revealed no trace elements which were consistently present and which suggested regular spatial variation in the vein. Splits of one of the barite samples were submitted as a blind check of laboratory precision. The analyses on the splits were identical for all elements except copper, lead and silver, all of which could have been contributed by traces of sulfide grains in the samples. The laboratory precision on the barite samples is believed to be adequate.

Two galena samples contained no measurable trace elements other than copper and silver. The copper could be present as admixed chalcopyrite and/or tetrahedrite and it was concluded that copper was not a suitable trace element to use in an attempt to define zoning. The emission spectrographic analyses revealed silver contents of 90 and 190 ppm in the two galena samples. Atomic absorption analyses of splits of the same galena samples revealed silver contents of 450 and 250 ppm respectively and the emission spectrography is adjudged to be too inaccurate for a detailed study of silver in galena. The erratic distribution of the silver in galena, as revealed by a comparison of the atomic absorption and electron microprobe results, precludes the use of silver in galena as a means to define trace element zoning in the Puzzle vein.

It is possible that one or more useful trace elements is present in one or more of the hypogene minerals and that such trace elements could be used to define zoning. Such trace elements, if present, are below the detection limits of the emission spectrography. The preliminary results were not promising, however, and no further work to study trace element zoning was undertaken.
LEAD ISOTOPE ANALYSES

ANALYSIS OF GALENA FROM THE PUZZLE VEIN

Four samples of galena were analyzed for lead isotope composition in an attempt to elucidate the genetic history of the lead in the Puzzle vein. A fifth sample was submitted for analysis as a blind check on laboratory precision. Splits of these samples were also analyzed for sulfur isotope composition and silver content. Polished grain mounts and X-ray diffraction analyses provided a check on sample purity. In all of the following discussion of the genetic implications of the lead isotope data it should be stressed that the conclusions pertain to only the lead separate and not to the other metallic components of the vein.

The lead isotope analyses were performed by Isotopes, Inc., of Westwood, New Jersey, using a 12 inch, 60 degree mass spectrometer. Details of sample treatment and analysis are given in Appendix D. The analytical results expressed in both percentages and ratios of $\text{Pb}^{206}/\text{Pb}^{204}$, $\text{Pb}^{207}/\text{Pb}^{204}$ and $\text{Pb}^{208}/\text{Pb}^{204}$ are tabulated below in Table 5. The lead isotope ratios for volcanic rocks in the Creede area are given in Table 8.

**TABLE 5 LEAD ISOTOPE ANALYSES OF GALENA**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>27.22</th>
<th>50.22</th>
<th>84.221</th>
<th>84.222</th>
<th>112.22*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb&lt;sup&gt;204&lt;/sup&gt;</td>
<td>1.384</td>
<td>1.373</td>
<td>1.351</td>
<td>1.360</td>
<td>1.377</td>
</tr>
<tr>
<td>Pb&lt;sup&gt;206&lt;/sup&gt;</td>
<td>26.052</td>
<td>26.049</td>
<td>25.884</td>
<td>25.922</td>
<td>26.032</td>
</tr>
<tr>
<td>Pb&lt;sup&gt;208&lt;/sup&gt;</td>
<td>51.254</td>
<td>51.295</td>
<td>51.504</td>
<td>51.398</td>
<td>51.302</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>206/204</th>
<th>207/204</th>
<th>208/204</th>
<th>207/206</th>
</tr>
</thead>
<tbody>
<tr>
<td>206/204</td>
<td>18.826</td>
<td>18.968</td>
<td>19.158</td>
<td>19.062</td>
</tr>
<tr>
<td>207/204</td>
<td>15.400</td>
<td>15.498</td>
<td>15.736</td>
<td>15.678</td>
</tr>
<tr>
<td>208/204</td>
<td>37.039</td>
<td>37.352</td>
<td>38.120</td>
<td>37.795</td>
</tr>
<tr>
<td>207/206</td>
<td>0.8180</td>
<td>0.8171</td>
<td>0.8214</td>
<td>0.8225</td>
</tr>
</tbody>
</table>

*Sample number 112.22 is a duplicate of number 50.22 and was submitted to check analytical precision.
The precision of the lead isotope analyses is stated to be ± 0.11 for the ratios 206/204 and 207/204 and ± 0.23 for the ratio 208/204 according to R. Senechal of Isotopes, Inc. (1969, written communication). These precisions are based upon standard deviations from mean isotope ratios calculated from ten replicate analyses of a single sample. The reproducibility of samples 50.22 and 112.22, which are duplicates, is considerably better than the precision quoted above and the analytical results on all of the galena samples from the Puzzle vein are considered valid.

The arithmetic means of the lead isotope ratios for the samples of galena from the Puzzle vein are 19.0035 for Pb\(^{206}/\text{Pb}^{204}\), 15.5780 for Pb\(^{207}/\text{Pb}^{204}\) and 37.5765 for Pb\(^{208}/\text{Pb}^{204}\).

**MODEL AGE CALCULATIONS**

The lead isotope composition of the Puzzle vein galena has been used to calculate model ages using several different mathematical models. The models are listed in Table 6 and the age results in Table 7. A detailed treatment of the mathematical and geological assumptions which underlie these models is included in Russell and Farquhar (1960, p. 44-59).

Three models are most commonly used to calculate ages of galenas from their lead isotope composition. These models are termed the Holmes-Houtermans, Russell-Farquhar-Cumming and Russell-Stanton-Farquhar models. Each model is based upon implicit and explicit assumptions of the evolution of the various lead isotopes throughout the history of the earth. The various models differ significantly in the assumptions regarding lead genesis.

The Holmes-Houtermans method assumes that all lead has grown from primeval lead in a deep source region. The lead isotope composition in
TABLE 6  MATHEMATICAL MODELS FOR LEAD ISOTOPE AGE CALCULATIONS

Holmes-Houtermans model -
\[
y - b_o = e^{\lambda t_o} - e^{\lambda t}
\]
\[
x - a_o = (137.8)(e^{\lambda t_o} - e^{\lambda t})
\]

Russell-Farquhar-Cumming model -
\[
x = a - 137.8V(e^{\lambda t} - 1)
\]
\[
y = b - V(e^{\lambda t} - 1)
\]
\[
z = c - W(e^{\lambda t} - 1)
\]

Russell-Stanton-Farquhar model -
\[
x = (137.8)(3.063 - e^{\lambda t})
\]
\[
y = (241.2)(e^{\lambda t})
\]
\[
z = 38.80 - 34.2(e^{\lambda t} - 1)
\]

\[x = \text{Pb}^{206}/\text{Pb}^{204}\] at time t, the age of galena formation
\[y = \text{Pb}^{207}/\text{Pb}^{204}\] at time t, the age of galena formation
\[z = \text{Pb}^{208}/\text{Pb}^{204}\] at time t, the age of galena formation

\[a_o = \text{Pb}^{206}/\text{Pb}^{204}\] in primeval lead = 10.36
\[b_o = \text{Pb}^{207}/\text{Pb}^{206}\] in primeval lead = 9.50
\[a = \text{Pb}^{206}/\text{Pb}^{204}\] in modern terrestrial lead = 18.80
\[b = \text{Pb}^{207}/\text{Pb}^{206}\] in modern terrestrial lead = 15.82
\[c = \text{Pb}^{208}/\text{Pb}^{204}\] in modern terrestrial lead = 39.10

\[\lambda = (0.1537)(10^{-9})/\text{year}, \text{ the decay constant for } \text{U}^{238}\]
\[\lambda = (0.9722)(10^{-9})/\text{year}, \text{ the decay constant for } \text{U}^{235}\]
\[\lambda = (0.0499)(10^{-9})/\text{year}, \text{ the decay constant for } \text{Th}^{232}\]

\[t_o = (4.51)(10^9) \text{ years, the age of the earth}\]
\[V = \text{U}^{235}/\text{Pb}^{204}\] at the present time = 11.0
\[W = \text{Th}^{232}/\text{Pb}^{204}\] at the present time = 40.8
The source region has changed with time due to the addition of radiogenic lead produced through the decay of uranium and thorium. The Pb\(^{206}\), Pb\(^{207}\) and Pb\(^{208}\) are daughter products of U\(^{238}\), U\(^{235}\) and Th\(^{232}\) respectively.

The lead in any galena is produced by transfer from the deep source and emplacement without contamination by lead from crustal rocks. The distribution of uranium and thorium in the deep source region is presumed to be homogeneous. Following crystallization of galena the isotope abundances are frozen and not subject to later change.

The Russell-Farquhar-Cumming model assumes that any galena contains lead from a source which is homogeneous with respect to its lead isotope composition. The source region for the Russell-Farquhar-Cumming model could be either the mantle or a portion of the crust which has become homogeneous by remelting and mixing. The lead, thorium and uranium in this model need not be derived solely from primeval lead, thorium and uranium plus radiogenic additions of lead in the deep source region, but may include lead derived from radiogenic decay in the crust prior to homogenization. The final transfer, emplacement and post-crystallization history of the lead would be similar to that of the Holmes-Houtermans model.
The Russell-Stanton-Farquhar model is designed to date galena from a particular type of deposit; conformable deposits formed by volcanic-exhalative processes from ore fluids which have not been contaminated by lead from crustal rocks. The Russell-Stanton-Farquhar model is of interest in the present study for purposes of comparison with the other models and because it allows calculation of a model age based only on the thorium-derived Pb\(^{208}\). In the Russell-Stanton-Farquhar model, as in the Holmes-Houtermans model, the lead in a galena is assumed to have come from a sub-crustal source region which has a homogeneous lead, thorium and uranium composition. The Russell-Stanton-Farquhar model differs from the Holmes-Houtermans model in that the former derives a growth curve empirically from both the lead isotope ratios in primeval lead and the ratios in modern lead, whereas the latter uses a growth curve based upon only the primeval abundances of the various isotopes. The Russell-Stanton-Farquhar model requires the lead growth curve to pass through analyzed values for the deposits at Bathurst, New Brunswick, deposits whose presumed genesis fits the model. Transfer, emplacement and post-crystallization history are similar to the other models.

The ages of each of the samples have been calculated using each of the three models and the results are given in Table 7. The equations for Pb\(^{206}/\)Pb\(^{204}\) and Pb\(^{208}/\)Pb\(^{204}\) are used for the Russell-Farquhar-Cumming model. The equations for Pb\(^{206}/\)Pb\(^{207}\) and Pb\(^{208}\) are used for the Russell-Stanton-Farquhar model.

It is immediately apparent from the model ages that the galena from the Puzzle vein has a variable and anomalous lead isotope composition. The identification of this galena as anomalous requires further explanation as the terminology and criteria for anomalous galena are ambiguous.
Houtermans noted two classes of anomalous leads; his J-type leads are those which are excessively radiogenic and give negative model ages. Houtermans' B-type leads are those which give positive model ages older than the enclosing rocks (Russell and Farquhar, 1960, p. 61). Russell and Farquhar have redefined anomalous leads to include only those which are excessively radiogenic, i.e., Houterman's J-type. The model ages of the Puzzle vein galena are clearly anomalous irregardless of the model applied and irrespective of the definition employed (Russell and Farquhar, op. cit.).

Cannon and Pierce (1967, p. 381) have used the ratio of Pb$^{206}$ plus Pb$^{207}$ plus Pb$^{208}$ to Pb$^{204}$, i.e., the ratio of radiogenic lead to Pb$^{204}$, to define the J-ness value of a sample and this value is used as a means of classifying lead isotope data. The arithmetic mean J-ness for the Puzzle galena is 72.16 which falls in the range of ordinary lead from other areas even though the Puzzle galena is clearly anomalous. The J-ness of 72.16 is clearly outside of the 75-81 range of J-type leads. It could be said that the galena from the Puzzle vein is anomalously anomalous.

ANALYSIS OF VOLCANIC ROCKS

The close temporal and spatial association of the Creede ore deposits and the volcanic host rocks necessitates a comparison of their respective isotopic compositions. The lead isotope composition of volcanic rocks in the Creede area has been determined by Doe (1968, p. 158) as shown below in Table 8.

The data from the rock lead analyses shown in Table 8 and the ore lead analyses shown in Table 5 are plotted in figure 24. It should be
Figure 24 Comparison of lead isotope analyses of ore lead from the Puzzle vein (o) and rock lead (x); large crosses indicate laboratory precision. Rock lead after Doe (1968, p. 158). Numbers adjacent to circles are sample numbers.
TABLE 8 LEAD ISOTOPE RATIOS OF VOLCANIC ROCKS
(after Doe, 1968, p. 158)

<table>
<thead>
<tr>
<th>Formation</th>
<th>Pb206/Pb204</th>
<th>Pb207/Pb204</th>
<th>Pb208/Pb204</th>
</tr>
</thead>
<tbody>
<tr>
<td>Willow Creek Member of Bachelor Mountain Rhyolite</td>
<td>18.74</td>
<td>15.63</td>
<td>38.09</td>
</tr>
<tr>
<td>Fisher Quartz Latite</td>
<td>18.36</td>
<td>15.58</td>
<td>37.68</td>
</tr>
<tr>
<td>Hinsdale Formation</td>
<td>18.38</td>
<td>15.62</td>
<td>38.26</td>
</tr>
</tbody>
</table>

recalled that the Bachelor Mountain Rhyolite is the host rock for the Puzzle vein, the Fisher Quartz Latite is the youngest major volcanic unit in the Creede area and the Hinsdale Formation is probably post-mineralization in age. The only published lead isotope data for galena from Creede is that of Doe and others (1966, p. 54). Galena from an unspecified locality in the Creede district contained Pb206/Pb204 of 19.15–19.22 and Pb208/Pb204 of 39.0 (Doe and others, op. cit.). Doe's result for Pb206/Pb204 is slightly higher than most of the Puzzle vein samples and his Pb208/Pb204 value is significantly higher than that of the galena from the Puzzle vein.

The ranges of Pb207/Pb204 and Pb208/Pb204 for the Puzzle vein galena overlap the ranges of these ratios for the volcanic rocks as shown in figure 24, whereas the ranges of Pb206/Pb204 are significantly different. These relationships are surprising in view of the fact that both Pb206 and Pb207 are derived from the same process, decay of uranium isotopes. The disparity of the Pb206/Pb204 values in galena and the volcanic rocks is taken as evidence that the lead from these two sources is not genetically related, a conclusion in accord with Doe (1968, p. 164).
similarity of the Pb$^{208}$/Pb$^{204}$ ratios, is considered to be fortuitous although many more analyses will be needed of both the volcanic rocks and galena before the relationship is certain.

**INTERPRETATION**

The most important single genetic conclusion that can be derived from the anomalous character of the Puzzle vein lead is that it did not evolve in a single closed system of homogeneous uranium and thorium content prior to emplacement at the end of the late Tertiary volcanism. The present isotopic composition of the galena necessitates contamination of primeval lead from the deep source region with radiogenic lead from the earth's crust. In an effort to further develop a model of lead genesis the isotopic results given in Table 7 will be used to calculate a two-stage model of evolution.

Since the final emplacement of galena in the vein did not occur later than the present, the formula $R = e^{\frac{\lambda t}{137.8}} - 1/137.8(e^{\frac{\lambda t}{137.8}} - 1)$ can be used to calculate the upper limit to the age of whatever rocks contained the uranium that provided the radiogenic lead (Russell and Farquhar, 1960, p. 65). $R$ in this formula represents the slope of a plot of Pb$^{207}$ versus Pb$^{206}$ and $t$ is the upper limit to the age of the source rocks (figure 24). The other symbols in this formula are described in Table 6. It should be noted that the formula for the age of the source rocks utilizes only the uranium-derived lead isotopes and does not take into consideration the thorium-derived lead. In making calculations of this type it should be emphasized that a two-stage model of lead evolution is assumed. The first stage presupposes lead evolution in a deep source region, presumably the mantle, which has a uniform uranium and thorium content. The second
stage involves evolution of uranium in the crust during a finite period of time prior to final emplacement of the lead as galena in the Puzzle vein. Both of these evolutionary stages are assumed to have occurred in closed systems, a very stringent assumption from the geologic standpoint. There is a decided tendency to interpret lead isotope data with the simplest conceivable model in a fashion analogous to geophysical interpretation of magnetic anomalies although the fit of a simple model does not preclude the possibility that the evolutionary path of a galena was really much more complicated.

The calculation of $t$ varies depending upon the slope of the $\text{Pb}^{207}$ versus $\text{Pb}^{206}$ curve which is chosen. Using samples 84.221 and 84.222, $R$ is 0.60 and $t$ is calculated to be 138 million years. Using the sample pair which maximizes $R$, the age is calculated to be 151 million years. The calculation of the maximum age of the rocks which are the source of the radiogenic lead can be further refined by assuming that the galena emplacement in the Puzzle vein is the same age as the adularia in the OH vein at Creede, i.e., 26 million years. Using this assumption the formula $R = (e^{\lambda t} - e^{\lambda t})/(137.8)(e^{\lambda t} - e^{\lambda t})$ can be applied. The 26 million year minimum age of emplacement is represented in the formula by $t$. If the 0.60 value for $R$ is applied the calculated value for the maximum age of the source rocks is 135 million years. The results of these calculations, while somewhat variable due to the uncertainty in the time of galena emplacement in the Puzzle vein, indicate that the uranium derived radiogenic lead evolved in rocks of probable post-Paleozoic age. It should be stressed that the conclusion regarding the age of the source rock for the radiogenic lead is based upon the assumption of a two stage model of lead evolution. The geological fit of the calculated age of the source rock is discussed below.
The values for Pb\(^{208}/\text{Pb}\(^{204}\) in the galena samples from the Puzzle vein are surprisingly low. The arithmetic mean value for the ratio of Pb\(^{208}\) to Pb\(^{204}\) is 37.5765. Table 7 lists model ages for the Pb\(^{208}\) component of the galena samples ranging from +394 to +1004 million years. Any model of lead isotope evolution must account for the unusually low thorium derived Pb\(^{208}\) abundance compared to the slightly radiogenic uranium derived Pb\(^{206}\) and Pb\(^{207}\) abundances. The Pb\(^{208}\) ages suggest that some of the lead in the galena was initially transferred from a deep source region in Precambrian time and emplaced as common lead in order to preserve the low Pb\(^{208}/\text{Pb}\(^{204}\) ratio. The common lead from a Precambrian host rock would be selectively remobilized later in order to avoid contamination with Pb\(^{208}\) from crustal rocks. The postulated retention of some of the lead as common lead in Precambrian rocks is necessary to explain the low Pb\(^{208}/\text{Pb}\(^{204}\) ratio as even ordinary lead of post-Precambrian age is higher in Pb\(^{208}/\text{Pb}\(^{204}\) than the Puzzle vein galena.

The remobilization of lead from the Precambrian host rock may have been concomitant with Oligocene volcanism. During the second stage transfer process from the Precambrian environment to the final depositional site in the Puzzle vein, radiogenically derived Pb\(^{206}\) and Pb\(^{207}\) must have been added. The source of the radiogenic Pb\(^{206}\) and Pb\(^{207}\) was, of necessity, an environment with a very low thorium to uranium ratio in order to avoid contamination with Pb\(^{208}\).

A more complex three stage model can be developed to explain the added radiogenic Pb\(^{206}\) and Pb\(^{207}\). The common lead from the Precambrian host rock could have been emplaced as common lead in a host rock of post-Precambrian age prior to final remobilization and final emplacement during Oligocene volcanic activity. The lead isotope data allow no choice
between the two stage model and more complicated models but the require-
ment of any model to maintain a low Pb$^{208}$/Pb$^{204}$ ratio in the final lead
composition makes more complicated models less probable.

The models of lead evolution for the galena from the Puzzle vein must
be compared to the geological history of the surrounding region in order
to test the geological feasibility of the mathematical models. The pro-
posed models involve either two or more stages. The first stage involves
initial evolution in a deep source region, presumably the mantle, and
subsequent transfer to a depositional site as common lead in a Precambrian
host rock. The second stage consists of retention of the lead for a con-
siderable period of time until remobilization results in transfer to an-
other depositional site. The depositional site following the remobiliza-
tion is either the Puzzle vein or a host rock of post-Precambrian and pre-
Tertiary age. The remobilization must have been selective in order to
avoid significant contamination with Pb$^{208}$ from the Precambrian environment.
Any minor contamination and mixing with Pb$^{208}$ from a crustal source during
the second stage transfer process would make the time of first stage re-
mobilization from the deep source region older.

Precambrian tectonic events which might be correlated with the trans-
fer from the deep source region are periods of granitic intrusion in south-
western Colorado which have been dated at 1350-1450 and 1700-1750 million
years (Tweto, 1968, p. 558). Alternatively the transfer of lead during
the first stage could have occurred during volcanism preceding the 1700-
1750 million year period of orogeny. The isotopic evidence provides no
basis for a choice among these or other alternative histories.

The remobilization and transfer from the Precambrian host rock to a
post-Precambrian and pre-Tertiary host rock, as envisaged by the three stage model, can be correlated with only one period of orogenic activity, the Laramide orogeny which has been tentatively dated at 65-70 million years in southwest Colorado (Tweto, 1968, p. 562). The possible host rocks of post-Precambrian age in the San Juan area are Jurassic and Cretaceous sedimentary strata. The host rocks of Jurassic or Cretaceous age must have had a low thorium to uranium ratio. A review of the thorium and uranium contents of various crustal rock types has been made for comparison with the source region of the uranium derived radiogenic lead isotopes. Hem (1959, p. 7) indicates that average thorium:uranium ratios are approximately 3.0:1 for igneous rocks, 5.1:1 for resistate sedimentary rocks, 8.4:1 for hydrolyzate sedimentary rocks and 0.85:1 for precipitate sedimentary rocks. Mason (1958, p. 44) gives uranium and thorium abundances which reveal an average thorium:uranium ratio of 5:1 for all crustal rocks. The calculated value of this ratio for the earth's mantle is 4:1 based upon the lead isotope values in ordinary lead. From these generalized data it appears that the source rock which could produce the required radiogenic addition of Pb206 and Pb207 without the addition of appreciable Pb208 is most likely a precipitate sedimentary rock such as a carbonate or evaporite. It is noteworthy that the requisite lithology is present in the Jurassic and Cretaceous sedimentary section which probably underlies the Creede mining district. The Jurassic or Cretaceous source of the radiogenic lead is evaluated further in the section on source of the ore-forming components.

The simpler two stage model of evolution can be invoked to explain the lead isotope composition of the galena from the Puzzle vein in a manner which is consistent with the geologic environment discussed above.
for the three stage model. The requisite uranium-derived radiogenic lead could be derived from the Jurassic or Cretaceous carbonate or evaporite lithology during upward passage of the ore-forming fluid or fluids from the Precambrian host rock to the final depositional site in the Puzzle vein without intermediate redeposition in a post-Precambrian and pre-Tertiary host rock.

It is apparent that the geological history of the San Juan region permits no choice between the two and three stage histories of lead evolution. In the three stage model the lead in the Precambrian environment would have been remobilized during Laramide tectonic and igneous activity and deposited in a host rock of probable Jurassic or Cretaceous age. In the two stage model the lead in the Precambrian host rock would not have been remobilized or altered in isotopic composition during the Laramide orogeny. The discussion of the lead isotope history has involved only the simplest mathematical and geological treatment of the data. The discussion has in no way eliminated the possibility of more complex histories.

The multi-stage history of lead evolution and the necessity to add lead from a crustal source are consistent with the sulfur isotope data in the following section. The sulfur isotope data can best be explained by a mechanism involving contamination of the ore-forming fluid or fluids with sulfur from crustal rocks.
Thirty sulfur isotope analyses were obtained on various hypogene sulfide and sulfate minerals in the Puzzle vein in an attempt to deduce the source of the sulfur. Twenty four of the samples were sulfides and six were barite. Two of the sulfide samples were duplicates submitted as a blind check on laboratory precision as noted in Table 9. The sulfide samples consisted of six galena samples, seven sphalerite samples, five pyrite samples, two tetrahedrite samples and four chalcopyrite samples. The samples were selected to represent the paragenetic sequence, to provide a distribution throughout the lateral and vertical extent of the vein as exposed to date, to provide a cross-section of the vein at a single site where the layering and depositional sequence was particularly well developed, and to analyze coexisting and contemporaneous mineral pairs to test for equilibrium deposition. At the intersection of the East strand and the Puzzle vein on the 9360 level the paragenetic sequence is particularly well developed through symmetrical layering of the vein minerals. At this locality it was possible to sample barite, galena, chalcopyrite and tetrahedrite for sulfur isotope analyses; from the walls inward the sequence of deposition is represented by samples 84.21 (barite), 84.221, 84.222 and 86.22 (galena), 84.25 and 86.25 (chalcopyrite) and 84.24 and 86.24 (tetrahedrite).

The results of the sulfur isotope analyses are shown in Table 9 and figure 25. All results are expressed as $\delta^{34}S$, i.e., as permil values, which are calculated as shown in the following equation:
### TABLE 9 SULFUR ISOTOPE ANALYSES

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Mineral</th>
<th>$\delta^{34}S_{\text{per}}$, permil</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.22</td>
<td>Galena</td>
<td>+ 3.81</td>
</tr>
<tr>
<td>50.22</td>
<td></td>
<td>- 0.94</td>
</tr>
<tr>
<td>84.221</td>
<td></td>
<td>+ 3.80</td>
</tr>
<tr>
<td>84.222</td>
<td></td>
<td>+ 3.10</td>
</tr>
<tr>
<td>86.22</td>
<td></td>
<td>+ 8.80</td>
</tr>
<tr>
<td>*112.22</td>
<td></td>
<td>+ 0.42</td>
</tr>
<tr>
<td>43.26</td>
<td>Sphalerite</td>
<td>+ 0.55</td>
</tr>
<tr>
<td>44.26</td>
<td></td>
<td>+ 0.38</td>
</tr>
<tr>
<td>121.261</td>
<td></td>
<td>- 1.07</td>
</tr>
<tr>
<td>143.261</td>
<td></td>
<td>- 0.17</td>
</tr>
<tr>
<td>143.262</td>
<td></td>
<td>+ 2.28</td>
</tr>
<tr>
<td>**143.263</td>
<td></td>
<td>+ 0.54</td>
</tr>
<tr>
<td>143.264</td>
<td></td>
<td>+ 1.02</td>
</tr>
<tr>
<td>1.23</td>
<td>Pyrite</td>
<td>- 0.04</td>
</tr>
<tr>
<td>47.23</td>
<td></td>
<td>- 8.26</td>
</tr>
<tr>
<td>54.231</td>
<td></td>
<td>- 1.35</td>
</tr>
<tr>
<td>54.232</td>
<td></td>
<td>- 0.72</td>
</tr>
<tr>
<td>61.23</td>
<td></td>
<td>+ 1.18</td>
</tr>
<tr>
<td>84.24</td>
<td>Tetrahedrite</td>
<td>- 1.45</td>
</tr>
<tr>
<td>86.24</td>
<td></td>
<td>+ 0.54</td>
</tr>
<tr>
<td>1.25</td>
<td>Chalcopyrite</td>
<td>+ 0.06</td>
</tr>
<tr>
<td>41.25</td>
<td></td>
<td>- 3.44</td>
</tr>
<tr>
<td>84.25</td>
<td></td>
<td>- 2.90</td>
</tr>
<tr>
<td>86.25</td>
<td></td>
<td>+ 0.42</td>
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<td>56.21</td>
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<td>84.21</td>
<td></td>
<td>+21.32</td>
</tr>
<tr>
<td>85.21</td>
<td></td>
<td>+20.73</td>
</tr>
</tbody>
</table>

*Split of sample No. 50.22 for precision check

**Split of sample No. 143.262 for precision check
Figure 25 Sulfur isotope abundance in hypogene minerals in the Puzzle vein. Arrows indicate the arithmetic mean value for each category.
The standard is troilite from the Cañon Diablo meteorite which has an $S^{34}/S^{32}$ ratio of 0.0450045. The troilite standard is arbitrarily assigned a $\delta^{34}S$ value of zero. Details of the analytical method are given in Appendix E. Sample purity for the sulfur isotope samples was checked by the use of polished grain mounts and X-ray diffraction analyses.

The laboratory precision of sulfur isotope analyses is stated to be ±0.10 permil (Jensen, 1967, p. 145). Duplicate analyses on pairs of galena and sphalerite samples showed differences of 1.36 and 1.74 permil respectively although most of these differences are believed to be due to sample inhomogeneity. There is evidence, discussed below, of marked disequilibrium in the sulfur isotope composition of the sulfide minerals and this disequilibrium is adjudged to be part of the reason for the sample inhomogeneity. Laboratory precision is believed to be adequate for the conclusions and interpretations discussed below.

The 24 sulfide samples range from +8.80 to -8.26 permil with an arithmetic mean of +0.298 and a median value of ±0.24 permil. These average values are very close to the meteoritic standard of zero permil and further statistical treatment of the data is warranted in order to evaluate the reliability of the average values. The standard deviation of the sulfide samples is ±2.35 permil. To test the reliability of the mean the Student-t test is applied (Freund, 1967, p. 225). For a 95 percent confidence limit the error, in the mean value for the sulfide samples of ±0.298 permil, is ±0.991 permil. For a 99 percent confidence limit the error in the mean is ±1.344 permil.
The arithmetic mean permil values for the various sulfide minerals are +3.165 for galena (six samples), +0.504 for sphalerite (seven samples), -1.838 for pyrite (five samples), -0.455 for tetrahedrite (two samples) and -1.465 for chalcopyrite (four samples).

The six barite samples have sulfur isotope values ranging from +17.00 to +23.94 permil with an arithmetic mean value of +20.08 which is very close to the value of +20.4 for ocean water sulfate. The Student-t test for reliability of the mean reveals a 95 percent confidence limit of +2.395 permil and a 99 percent confidence limit of ±3.605 permil.

The most apparent feature of the sulfur isotope results is the marked bimodal distribution of values with sulfide minerals near zero permil and barite near 20.4 permil.

There appears to be a slight tendency towards enrichment of the sulfide minerals in $\delta^{32}$S as deposition proceeded in time. The early sulfide minerals, galena and sphalerite, have a sulfur isotope composition ranging from +8.80 to -1.07 with an arithmetic mean of +1.73 permil. The later sulfide minerals, chalcopyrite, tetrahedrite and pyrite, range from +1.18 to -8.26 with an arithmetic mean of -1.45 permil. Standard deviations are 2.41 and 2.40 for the earlier and later sulfides respectively and these relatively large deviations preclude further interpretation of the apparent change in permil sulfur isotope values with time.

**INTERPRETATION**

Several of the analyses tested the possibility of sulfur isotope zoning in hand specimens of layered pyrite and sphalerite. Samples 143.261, 143.262, and 143.264 represent a sequence of sphalerite deposition from oldest to youngest. Samples 54.231 and 54.232 represent
successive deposition of botryoidal pyrite with 54.232 being the younger. There is no apparent zoning trend of sulfur isotope values in these hand specimens and the disequilibrium deposition of sulfur isotopes, as discussed below, makes it unlikely that a zoning trend in hand specimens exists.

There is no apparent zoning of sulfur isotope values in a particular mineral in space although the relatively small number of analyses for any single mineral does not allow an adequate test for the present or absence of spatial zoning.

Coexisting sulfide mineral pairs were submitted for analysis as a test of equilibrium hypogene deposition in the Puzzle vein. Previous workers have found systematic variations in the permil values of coeval and coexisting sulfide mineral pairs. These systematic variations have been attributed to isotopic fractionation due to differing bond strengths of the sulfur-metal bonds (Stanton and Rafter, 1967, p. 1091 and Bachinski, 1969, p. 56). The predicted fractionation effects for equilibrium conditions indicate that pyrite should be preferentially enriched in $\delta^{34}S$ compared to chalcopyrite whereas the reverse is shown by these minerals in the Puzzle vein. The predicted sequence from greatest to least enrichment in $\delta^{34}S$ is pyrite–sphalerite–chalcopyrite–galena (Bachinski, 1969, p. 56). Sphalerite should be enriched in $\delta^{34}S$ relative to galena although the reverse is true for these minerals in the Puzzle vein. The sulfur isotope data suggest that equilibrium deposition of sulfide minerals did not occur in the Puzzle vein. It should be stressed that this discussion of equilibrium pertains only to equilibrium between the sulfur species in the ore fluid and the sulfide minerals being deposited. In the section on mineralogy it was noted that sphalerite and galena form alternating
layers with essentially contemporaneous barite. The preponderance of barite in the Puzzle vein is important in the context of equilibrium versus disequilibrium in the sulfide minerals. The partitioning of sulfur isotopes between the sulfate and sulfide minerals during the course of the alternating deposition of barite and sphalerite and galena may have precluded the attainment of equilibrium conditions.

The sulfur isotope data reveal a bimodal distribution of sulfide and sulfate mineral species with the sulfide sulfur centered on zero permil and the sulfate sulfur very near the value for ocean water sulfate. The bimodal nature of the sulfur isotope distribution necessitates a hydrothermal source fluid or fluids with a mean permil value in the range of +10 to +20; a fluid or fluids with the zero permil sulfur isotope composition typical of magmatic hydrothermal deposits could not produce the isotopically heavy barite which is present in the Puzzle vein.

Several geologic features of the Puzzle vein must be considered in arriving at a genetic interpretation of the sulfur isotope data. Barite is by far the most abundant vein mineral and barite is approximately one decimal order of magnitude more abundant than the total of all sulfide minerals in the Puzzle vein as exposed to date. The writer's impression in regard to zoning is that barite is decreasing in both relative and absolute abundance at depth in the Puzzle vein. Experience in the older mines of the Creede district has shown that barite becomes less abundant at depth. The zoning of barite in the Puzzle vein and elsewhere in the Creede district is discussed in detail below in the section on zoning. There is no evidence, however, that sulfide sulfur will exceed sulfate sulfur in the deeper and as yet unexposed part of the Puzzle vein even though barite appears to be decreasing in abundance at depth. Past
mining experience has shown that the veins of the Creede district bottom at an elevation of 9,100 - 9,200 feet. If the Puzzle vein bottoms at this depth the sulfur contained in barite will greatly exceed the total sulfur in sulfide minerals over the full extent of the vein. This conclusion takes into consideration the possibility that the vein may extend another mile to the north of the presently exposed north end of the Bull-dog Mountain mine and that the barite may decrease in abundance northward as well as downward.

In discussing the sulfur isotope data it is emphasized that barite is the predominant sulfur-bearing mineral in the vein and that the barite overlaps the abundant sulfide minerals, sphalerite and galena, in time of deposition.

Five hypotheses will be considered in analyzing the sulfur isotope data with reference to the ultimate source or sources of the sulfur. The first hypothesis is deposition of sulfur in sulfide and sulfate minerals in the Puzzle vein from a single fluid from a single source, with isotopic fractionation to produce the sulfate sulfur enriched in $^{34}$S and the sulfide sulfur enriched in $^{32}$S. The second hypothesis is deposition of the two sulfur modes from a single ore-forming fluid which has derived its sulfur content from two different sources during upward passage to the final depositional site, without mixing and equilibration of the sulfur from the different sources. The third hypothesis also involves two sulfur sources contributing to the sulfur content of a single fluid but with mixing, isotopic equilibration and later fractionation to produce the bimodal sulfur in the vein. The fourth and fifth hypotheses involve a mixing of two fluids, each containing sulfur, from two sources. The
fourth hypothesis invokes transport of the sulfur without isotopic mixing and homogenization, i.e., akin to the transport postulated in hypothesis two. The fifth hypothesis consists of isotopically different sulfur from two sources brought together by a mixing of fluids with subsequent isotopic equilibration and fractionation as proposed in hypothesis three.

The possibility of a mixing of fluids is difficult to evaluate. Mixing of hypogene and supergene fluids to produce the bimodal sulfur distribution is unlikely as there is no apparent source of sulfur for descending fluids and there is no evidence from wallrock alteration that fluids moved laterally into the vein. The possibility of a mixing of two or more hypogene fluids at depth is more likely but harder to evaluate.

In a study of fluid inclusions in sphalerite from the OH vein at Creede, Roedder (1960, p. 1337) concluded that the fluid was primary but that it was not possible to discriminate between changes of the fluid with time and mixing of fluids from two sources. It is unlikely that sulfur isotope data could be used to distinguish between a single hypogene fluid containing sulfur from two sources and a mixture of two fluids each with a characteristic sulfur isotope composition.

The first hypothesis involving sulfur isotopic exchange in a single fluid from a single source to produce the bimodal sulfur isotope distribution in the vein is considered unlikely. Such a fluid would need to contain sulfur with a permil value in the range of approximately +10 to +20 because of the predominance of barite in the vein. It seems extremely fortuitous that the fluid which formed the Puzzle vein would have the exact sulfur isotope composition to fractionate and produce sulfide minerals with the narrow spread of values and mean value at zero permil so characteristic of magmatic hydrothermal mineral deposits plus the sulfate
mineral with a narrow range of values and mean value near that of ocean water sulfate. There is no apparent single source for sulfur of the requisite composition, if the distribution of sulfur isotope values is to be explained by derivation of sulfur from a single source.

One of the four multiple source hypotheses is favored by the writer. The distribution of isotope values indicates that a mixing of magmatic sulfur from a deep source and sulfur from a marine sulfate in a shallow crustal environment has operated to produce the observed bimodal distribution. The sulfur isotope data do not permit a choice between a single fluid containing sulfur from two sources, and mixing of two fluids. The data also do not elucidate the transport mechanism of the sulfur from the two sources, with reference to mixing and isotopic equilibration versus transport of sulfur species of differing isotopic composition without mixing during transport.

The presence of the sulfate ion in fluid inclusions in sphalerite from the OH vein at Creede as noted by Roedder (1965, p. 38) is permissive evidence that the sulfate ion may have been present in the ore-forming fluid or fluids at depth. It is suggested that a sedimentary source may have furnished the sulfate which formed the barite and that the sulfate was transported to the site of vein deposition as a separate sulfur species. The sedimentary source may have been an evaporite bed and/or a connate brine in the sedimentary section of Mesozoic age which underlies the Creede district. The sulfur which is present in the sulfide minerals was transported from a deep source in the lower crust or mantle.

There is evidence, from a carbon and oxygen isotope study of travertine in the Creede Formation, that sedimentary carbonate in the Mesozoic
stratigraphic section was remobilized by magmatic activity during volcanism (Steven and Friedman, 1968, p. 833). In the section on lead isotope analyses it was concluded that lead from a sedimentary environment was added to the ore-forming fluid or fluids. The sulfur isotope data are interpreted to indicate a multiple source for the sulfur and it is noteworthy that the isotope data, for both lead and sulfur, suggest multiple sources for these elements. It is emphasized that two sources are required to explain the sulfur isotope analyses, irregardless of the manner in which the sulfur was carried in the ore-forming fluid.

Zoning in the Puzzle Vein

Sulfur isotope analyses failed to detect zoning of sulfur isotopes in hand specimens. The minerals barite and galena were analyzed by emission spectroscopy in an attempt to use trace elements in one of both of these minerals to define zoning in the Puzzle vein, as discussed in the section on trace chemical analyses. The emission spectroscopy revealed no consistent trace element content in either mineral which was useful in defining zoning. Followed-thin sections of sphalerite show an alternating sequence of lighter and darker layers in sphalerite which are presumably due to a variation in iron content. The distribution of sphalerite in the Puzzle vein is not sufficiently extensive, however, to permit the use of the zoning in iron content in sphalerite to define zoning over the spatial extent of the vein.

The distribution of optically visible minerals was mapped in drifts and cross-cuts with a view to test for the presence of zoning of minerals within the vein. Supplemental observations of mineral distribution
ZONING

Zoning which results from mineral deposition can be manifested on various scales, e.g., regional zoning, zoning within a particular mining district, zoning of minerals or trace elements within a single deposit and zoning within a single crystal. The present study investigated only zoning within the Puzzle vein and within individual hand specimens although the information derived from the Puzzle vein is used in conjunction with published data to aid in deriving a tentative zoning pattern for the Creede mining district.

ZONING IN THE PUZZLE VEIN

Sulfur isotope analyses failed to detect zoning of sulfur isotopes in hand specimens. The minerals barite and galena were analyzed by emission spectrography in an attempt to use trace elements in one or both of these minerals to define zoning in the Puzzle vein, as discussed in the section on trace chemical analyses. The emission spectrography revealed no consistent trace element content in either mineral which was useful in defining zoning. Polished-thin sections of sphalerite show an alternating sequence of lighter and darker layers in sphalerite which are presumably due to a variation in iron content. The distribution of sphalerite in the Puzzle vein is not sufficiently extensive, however, to permit the use of the zoning in iron content in sphalerite to define zoning over the spatial extent of the vein.

The distribution of megascopically visible minerals was mapped in drifts and cross-cuts with a view of test for the presence of zoning of minerals within the vein. Supplemental observations of mineral distribution
were made in stopes and on sub-levels. The supergene minerals are not abundant in most portions of the vein and no evidence of supergene zoning was noted. The following discussion involves only the hypogene minerals. Some of the hypogene minerals are widespread on both the 9360 and 9700 levels of the mine; quartz, barite, galena, sphalerite, pyrite and the hypogene variety of native silver fall into this group. The hypogene origin of some of the native silver is discussed in a later section. Other minerals including rhodochrosite and tetrahedrite were found only on the 9360 level although microscopic study revealed the presence of minor tetrahedrite in samples from the 9700 level.

There is a decrease in both the relative and absolute abundance of barite at the north end of the mine. At the north end of the 9360 level rhodochrosite and amethystine quartz appear to be increasing in abundance relative to barite. On the 9700 level pyrite becomes predominant at the north end of the level as barite decreases in both relative and absolute abundance. There are no apparent changes in either the relative or absolute abundance of galena or sphalerite with depth. The relative quartz content of the vein seems to be increasing at depth. Pyrite is widespread on both the 9360 and 9700 levels but it is much more abundant on the 9700 level. Chalcopyrite is more abundant on the 9360 level and it was noted on the 9700 level only at the north end of the mine.

The Bulldog Mountain mine probably has explored only a small part of the Puzzle vein. The north end of the vein has not been reached on either the 9360 or the 9700 level and the downdip extension below the 9360 level is untested. For these reasons it is premature to define a zoning pattern with any degree of confidence at the present time. The following tentative
Ideas are presented as a working hypothesis which can be tested as mine development proceeds.

The pattern of hypogene mineral distributions suggests that isograds can be drawn in the vein which rake to the south (figure 26). The rake of isograds based on mineral distributions is consistent with and essentially parallels the reconstructed land surface in the Creede mining district at the time of hypogene deposition (Steven, 1969, p. 696). It should be noted that the rake of the isograds is opposite to the northward rake of the south end of the vein. The rakes of both the zoning and the south end of the vein are consistent with an ore-bearing fluid or fluids having a southward as well as an upward movement, i.e., movement of the hypogene fluid or fluids perpendicular to the southward sloping land surface.

It is worthwhile to compare zoning and paragenesis in the Puzzle vein as they are both expressions of the same processes of and controls over ore deposition. The gangue minerals of the early rhodochrosite-quartz-barite-sphalerite-galena suite show a crude zonal arrangement. Rhodochrosite is abundant only at the north end of the 9360 level, the deepest part of the vein exposed to date. Quartz is most abundant, relative to barite, towards the north end of the 9360 level; quartz extends farther south and higher in the vein than rhodochrosite. Barite extends farther south and higher in the vein than quartz; barite is the only vein mineral on the uppermost 9940 level of the Bulldog Mountain mine. Thus it appears that the spatial arrangement of rhodochrosite, quartz and barite parallels the time sequence of their deposition with the earlier minerals lower and the later minerals higher in the vein. The vein formed from the bottom up during the early period of gangue mineral deposition.
Figure 26  Vertical longitudinal projection of the Puzzle vein showing the productive zone as exposed to date. Dotted lines represent the isograds of hypogene minerals in the vein.
Sphalerite, galena and the later minerals do not fit the zonal sequence described above. All of the sulfide minerals and hypogene native silver overlap the gangue minerals in space. The telescoping of the later part of the paragenetic sequence, in space, suggests that depositional conditions may have changed during the time span of vein formation.

In the section on the sequence of mineral deposition it was noted that a period of minor faulting intervened between the earlier rhodochrosite-quartz-barite-sphalerite-galena stage and the later chalcopyrite-tetrahedrite-pyrite stage. The spatial overlap of the gangue and sulfide minerals, as well as the evidence of faulting within the paragenetic sequence, suggests that vein deposition may have had a considerable time span. Further evidence of the time span and the separation of the paragenetic stages in time is the paucity of trace elements in native silver and the low silver content of galena and tetrahedrite; the chemistry of these minerals suggests that either the depositional environment or the composition of the ore fluid or fluids changed during vein formation.

In the following section, the tentative zoning pattern displayed by the distribution of hypogene minerals in the Puzzle vein will be compared to zoning patterns in parallel veins of the Creede district.
The pattern of hypogene mineral zoning in the Puzzle vein is consistent with published descriptions of mineral distributions in the older mines of the Creede district, although it should be stressed that published data are incomplete and based upon studies conducted after much of the ore had been removed.

By far the most productive and intensively studied vein in the Creede district is the Amethyst vein (figure 4). Emmons and Larsen (1923, p. 100) note that barite is abundant to the deepest levels of the Bachelor and Commodore mines, the southernmost mines on the Amethyst vein, although barite is not abundant in the deeper levels of the Last Chance and Amethyst mines in the middle portion of the vein and is still rarer in the deeper levels of the Happy Thought and Park Regent mines at the northern end of the Amethyst vein (figure 27). In the Bachelor mine at the south end of the Amethyst vein barite is especially abundant in the outcrop and on the higher levels of the mine (Emmons and Larsen, 1923, p. 146). This decrease in barite abundance northward and with increasing depth resembles the pattern which appears to be developing in the Puzzle vein. A similar pattern was noted in the Solomon-Holy Moses vein where barite was sparingly present in the upper levels on the vein but was not noted on the lower adit level of the Solomon mine (Emmons and Larsen, 1923, p. 100).

The presence of rhodochrosite in the Creede district has been previously noted only in the Amethyst mine on the Nelson tunnel level near the bottom of the Bachelor mine at an elevation of approximately 9125 feet (figure 27).
Figure 27 Vertical longitudinal projection of the Amethyst vein showing the distribution of ore. Modified after Emmons and Larsen, 1923, p. 127.
The distribution of native silver in the older mines at Creede is noteworthy. In the Amethyst vein native silver was especially abundant in the upper levels of the Bachelor, Commodore, Last Chance and Amethyst mines but was found to be less abundant farther north in the Happy Thought and Park Regent mines. A vertical longitudinal projection of the Amethyst vein shows the productive zone at the south end of the vein raking southwards, a pattern which resembles the tentative pattern in the Puzzle vein. In the Solomon and Holy Moses mines native silver was abundant only in the upper levels of the mines.

Emmons and Larsen (1923, p. 98, 116 and 117) considered native silver in the deposits they studied at Creede to be supergene in origin and if this conclusion is valid the distribution of native silver should not be used to define hypogene zoning. The evidence given by Emmons and Larsen (1923, p. 116 and 117), however, is not conclusive. The overall distribution of silver ore parallel to zoning of barite, which is clearly hypogene, in the Amethyst and Solomon-Holy Moses veins and the conclusions concerning the origin of the native silver in the Puzzle vein as stated herein suggest that the older geologic work at Creede should be re-evaluated concerning native silver genesis. In this regard it should be stressed that silver minerals characteristic of supergene silver ores such as acanthite and the halogen silver minerals have not been identified in the Amethyst and Solomon-Holy Moses veins.

The available evidence indicates that a poorly developed hypogene zoning pattern exists in the Creede mining district with zones raking southward towards the resurgently domed Creede caldera and the intrusive body which is believed to underlie the caldera. It should not be inferred
that the hypothetical intrusive is the direct source of the ore-forming fluids as there is tenuous evidence from the form of the Puzzle vein that the fluids were moving to the south as they ascended.
ENVIRONMENT OF HYPOGENE DEPOSITION

Depth

Any conclusions regarding the physico-chemical environment of hypo-gene mineral deposition must involve reconstruction of the land surface which existed at the time of deposition. Fortunately at Creede there is good geologic control of this surface. At the north end of the Bulldog Mountain fault the surface was probably marked by the slightly eroded top of the Nelson Mountain Quartz Latite at the time of vein formation (Steven, 1969, p. 696). The base of this formation, near the northern end of the Bulldog Mountain fault and about two miles north of the northernmost workings in the Bulldog Mountain mine is at an elevation of about 11,520 feet. The minimum thickness of the Nelson Mountain Quartz Latite at this locality is approximately 400 feet although the original thickness may have been somewhat greater. In this regard it should be recalled that the potassium-argon dating discussed above reveals that vein formation in the Creede district began at the close of the period of major volcanic eruption. It is unlikely that appreciable erosion occurred between the eruption of the volcanic formations and the onset of vein deposition. Thus the land surface two miles north of the mine workings at the time of ore deposition probably stood at about 12,000 feet, in terms of present elevations, although it may have been a few hundred feet higher.

The land surface farther to the south was probably lower and marked by the slightly eroded top of the Creede Formation. The topographically highest exposure of the Creede Formation at the present time, in the area
of the mines of the district, is 10,800 feet and this elevation repre-
sents a minimum for the surface over the Puzzle vein at the time of ore
deposition. The Creede Formation at the higher elevations in the dis-
trict is a coarse grained fluviatile facies which probably wedged out
away from the Creede caldera. It is not possible to give a reliable
estimate of the original thickness of the wedge edge in the vicinity of
the Bulldog Mountain mine. Similarly it is not possible to accurately
estimate the thickness of Creede Formation which had been eroded prior
to vein formation, although the eroded thickness was probably only a few
hundred feet. A best estimate would place the land surface over the
Puzzle vein at the time of ore deposition at an elevation of 11,300 ± 500
feet, in terms of present elevations. Thus it is seen that the land sur-
face sloped southwards towards the moat which encircled the Creede cal-
dera and formed the depositional basin for the lacustrine facies of the
Creede Formation. The projected outcrop of the Puzzle vein at the pre-
sent land surface ranges in elevation from 10,000 to 10,800 feet.

The highest exposure of veining on the Puzzle vein is on the 9940
level (Puzzle or Nickel Plate adit) where a barite vein has a maximum
thickness of two inches; no ore minerals were noted at this elevation.
The ore bodies currently being mined in the Bulldog Mountain mine have
been exposed at a maximum elevation of 9,800 feet although at this ele-
vation the ore shoots are short and discontinuous in a strike direction.
Most of the Puzzle vein lies below the 9700 level. It can be concluded
that the top of the ore bodies formed at a depth of 1,600 ± 500 feet
beneath the then extant land surface. A recent paper by White (1967,
p. 620) expressed the conclusion that the ore deposits of the Creede
district formed only a few hundred feet beneath the land surface which
existed at the time of deposition. Steven (1969, p. 696) has ably re-
jected White's conclusions with emphasis on the Amethyst and OH veins.
The present study supports Steven's conclusion that the Creede ores were
deposited at depths in excess of 1,000 feet and most of the Puzzle vein
probably formed at a depth greater than 1,500 feet.

Temperature

Several indirect lines of reasoning can be used to establish limits
on the temperature of vein mineral deposition in the Puzzle vein. Appli-
cation of the depth of formation and conjectural geothermal gradients
can be used to deduce a minimum temperature of formation. Gradients of
ten to fifty degrees Celsius per kilometer indicate a temperature at the
depth of ore formation of 5-25 degrees Celsius above mean surface
temperatures. Normal geothermal gradients, however, are certainly too
low because considerable heat would have been retained by the volcanic
host rocks which were geologically recent at the time of vein formation.

Studies of primary fluid inclusions in sphalerite from the OH vein
at Creede indicate a filling temperature of 190-265 degrees Celsius
these fluid inclusion studies are given below in the section on the
nature of the hypogene fluid.

The portion of the OH vein studied by Roedder is vertically and
mineralogically deeper than the Puzzle vein as presently exposed. There-
fore Roedder's work represents a maximum temperature of formation of the
Puzzle vein. The fluid inclusion temperatures represent a valid maximum
temperature for only the sphalerite deposition and the later chalcopyrite-
pyrite-tetrahedrite-native silver suite may have been deposited at signi-
ficantly different temperatures.
The ore minerals in the Puzzle vein do not exhibit any textural features such as exsolution phenomena which can be used for geothermometry. Hultta and Wright (1964, p. 1013) have studied the solubility of Ag₂S in the galena lattice at temperatures above 300 degrees Celsius. They have not suggested the use of their data as a geothermometer but Ag₂S solubility in galena is approximately linear over the range of 300–600 degrees Celsius. The solubility of Ag₂S in galena as a function of temperature may be expressed by the empirical relationship shown below:

\[ S = -0.311 + 0.00143 T \]

where \( S \) is solubility in mol percent and \( T \) is temperature in degrees Celsius. The electron microprobe data discussed above indicates that the Ag₂S content of galena from the Puzzle vein lies below about 0.023 mol percent. It is suggested that the linear solubility relationship and the maximum value for Ag₂S in galena from the Puzzle vein can be used to calculate a maximum temperature of formation for the galena. The application of the Ag₂S content of the galena and the solubility relationship gives a maximum temperature of formation of 234 degrees Celsius. Although such extrapolation to temperatures lower than 300 degrees Celsius is inherently dangerous because the linear nature of the solubility versus temperature plot will change, the calculation does provide a check on the fluid inclusion data.

The temperature dependency of the stability fields of several mineral pairs has been studied by Barton and Toulmin (1964) in relation to sulfur fugacity. It is suggested that the laboratory studies of temperature versus sulfur fugacity can be used in conjunction with the observable mineral assemblage of the Puzzle vein to estimate the maximum temperature of formation of the Puzzle vein. Figure 28 shows the temperature versus log of sulfur fugacity plot given by Barton and Toulmin (1964, p. 123).
Figure 28 Diagram of mineral equilibrium on a plot of log sulfur fugacity versus temperature. Shaded area represents stability field of coexisting pyrite and native silver. Abbreviations: Ag - native silver, ac - acanthite, bn - bornite, cp - chalcopyrite, gal - galena, Pb - native lead, po - pyrrhotite, and py - pyrite.

(Modified after Barton and Toulmin, 1964, p. 623).
Since pyrrhotite is absent from the Puzzle vein and acanthite (argentite) is rare, it is tentatively concluded that the temperature of formation during the deposition of the chalcopyrite-tetrahedrite-pyrite-native silver suite cannot be greater than the temperature of approximately 245 degrees Celsius at which the pyrite-pyrrhotite and acanthite-native silver lines cross. This reasoning is subject to the inherent difficulties involved in applying simple laboratory studies to natural geologic systems. Evidence has been given above that hypogene deposition of native silver followed pyrite deposition in time. It is entirely possible that the sulfur fugacity during native silver deposition was significantly lower than during pyrite deposition. A drop in sulfur fugacity under adiabatic conditions would permit pyrite deposition to be succeeded by native silver deposition at a temperature in excess of 245 degrees Celsius.

It is interesting to note that the maximum temperature of deposition deduced from the plot of the log of sulfur fugacity versus temperature is consistent with the temperature measured in fluid inclusions and also with the temperature calculated from the \( \text{Ag}_2\text{S} \) content of galena. The area of figure 28, within which both pyrite and native silver are stable, is well within the stability fields of galena and chalcopyrite and both of these minerals are widespread in the Puzzle vein.

Several types of evidence provide limits on the temperature of formation of the Puzzle vein. The silver content of galena is used to calculate a maximum temperature of 234 degrees Celsius. Fluid inclusions in sphalerite from the OH vein at Creede give maximum temperatures in the range of 190-265 degrees Celsius. The sulfur fugacity versus temperature
plot indicates a maximum temperature of 245 degrees Celsius. Geothermal gradients give a minimum temperature of vein deposition of 5-25 degrees Celsius above mean surface temperatures. It is concluded that the temperature of deposition of the Puzzle vein was most likely in the epithermal range of 50-200 degrees Celsius.

There is no direct evidence from the present study concerning the possibility and direction of temperature changes during vein formation. The telescoping of the paragenetic sequence in space, as discussed above in the section on zoning, is permissive evidence that the environment of deposition was cooling with time. Alternatively the telescoping could be due to changes in the composition of the ore-forming fluid or fluids.

Pressure

It is difficult to make any judgements regarding the pressure environment at the time of hypogene deposition. The fundamental uncertainty is the nature of the hydrothermal system. The fissure filling nature of the vein indicates that the system was open over the vertical interval of vein deposition. The fissure was incompletely filled in many areas of vein formation and an open fissure as much as one foot wide is still preserved. The Puzzle vein pinches upwards and circulation of the ore-forming fluids was no doubt retarded as they approached the surface. The ore depositional process involved neither a completely open nor a completely closed system but instead was intermediate between these two extremes. If the hydrothermal conduit was open the pressure at the depth of ore deposition can be considered to be the hydrostatic pressure at that depth or about 47.8 bars at the estimated 1,600 feet depth of
formation. In the partly closed system envisaged for the Puzzle vein in an area of explosive volcanic activity like the Creede district, it is easy to imagine that pressure on the hydrothermal fluid in excess of the hydrostatic pressure might have existed. It is not possible to quantitize this conjectural over-pressure.

There are few experimental data which can be used to estimate the pressure in the physico-chemical system in which the Puzzle vein formed. The fluid inclusion studies to date on vein deposits reveal that Cl is the dominant anion and Na is the dominant cation (Roedder, 1967, p. 548 and 551). Thus the system NaCl-H₂O may be a reasonable first approximation of the hydrothermal fluid. Fluid inclusion studies on sphalerite from the OH vein in the Creede district indicate a concentration of total salts of four to twelve percent with the sodium ion being the dominant cation and chloride ion being the dominant anion (Roedder, 1965, p. 381). An examination of the system NaCl-H₂O in terms of pressure and temperature indicates that the pressure at a temperature of 350 degrees and a composition of four to twelve percent NaCl is approximately 170 bars (figure 29). At the postulated lower temperature of formation of the Puzzle vein, a conjectural NaCl-H₂O fluid would be under an even lower pressure and possibly within the two phase region of liquid plus vapor. From the very crude estimates of pressure given above it seems likely that the pressure in the system which formed the Puzzle vein was in the range of 50-150 bars.

**Equilibrium**

The application of experimental data to field studies of ore deposits is valid only if equilibrium deposition can be adequately demonstrated.
Figure 29  Pressure-temperature-composition diagram of the system NaCl-H₂O. Modified after Roedder, 1967, p. 560.
The various solid phases in the Puzzle vein are definitely not in solid-solid equilibrium with each other. The compositional zoning displayed by the color layering in botryoidal sphalerite is clear evidence that solid state equilibrium does not exist in the sphalerite, even on a microscopic scale.

The sulfur isotope data discussed previously indicate that equilibrium was not attained between the sulfur isotope composition of the coeval mineral pairs sphalerite-galena and pyrite-chalcopyrite. The disequilibrium in the sulfur isotope compositions is disequilibrium between both the solid phases and the ore-forming fluid, and between the respective co-existing solid phases.

The well developed botryoidal texture of sphalerite on a microscopic scale and pyrite on a megascopic scale can be interpreted in terms of equilibrium versus disequilibrium deposition. Roedder (1968, p. 468) notes that the dominant parameter controlling the formation of botryoidal or "colloform" textures is a relatively high degree of supersaturation. A greater degree of supersaturation will increase the rate of new crystal nucleation and growth and thereby favor development of the botryoidal texture. An increase in supersaturation moves the system further away from equilibrium between the source fluid and previously deposited solid phases.

The compositional, textural and isotopic evidence noted above suggests that several types of partial equilibrium were not attained during the course of deposition of the Puzzle vein. In this regard it should be recalled that there is no textural evidence of post-depositional changes, such as sulfide remobilization, in the minerals of the Puzzle vein. There
is additional evidence, however, that suggests that equilibrium condi-
tions of deposition did prevail in a portion of the vein during at least 
some of the period of hypogene deposition. The hydrothermal leaching of 
large barite crystals followed by later deposition of smaller barite 
crystals at the same sites was described above and illustrated by 
figures 10 and 11. The hydrothermal fluid in these cases must have been 
in delicate equilibrium with the solid barite phase in such a fashion 
that deposition, leaching and renewed deposition occurred.

From the discussion of equilibrium a crude model of depositional 
conditions can be outlined. Near the bottom of the vein, as presently 
exposed, the deposition occurred under equilibrium conditions during at 
least part of the paragenetic interval. Higher in the vein towards the 
top of the open fissure the abundant massive and botryoidal pyrite marks 
the site of rapid deposition under conditions of supersaturation and 
marked disequilibrium (figure 7). Experience in the older and deeper 
mines of the Creede district has shown that the crystal size of galena 
and sphalerite increases with depth. This pattern of increasing crystal 
size with depth fits the concept of a closer approach to equilibrium 
between the ore-forming fluid and the solid phases at depth in the Puzzle 
vein. There is a slight apparent increase in crystal size in the Puzzle 
vein with depth over the relatively limited vertical range of the vein 
which has been exposed by mining to date.

**Nature of the hypogene fluid**

The temperature and pressure data discussed above for the hypogene 
environment indicates that the hydrothermal fluid was well within the 
two phase liquid plus vapor region. The deposition of vein minerals from
a liquid does not rule out earlier transport in a supercritical fluid phase.

The disequilibrium and increasing supersaturation of the ore-forming fluid as it progressed upwards could be due to one or more of several hypothetical conditions. Mixing of the ore fluid with groundwater could have caused rapid cooling which may have depressed solubilities in the hypogene fluid. Alternatively the normal upward progression of the hypogene fluid into cooler wall rocks could have caused a decrease in fluid temperature. A review of the mechanisms for cooling hydrothermal fluids by Barton and Toulmin (1961, p. D349) indicates that loss of heat by conduction into wallrock is unimportant in most veins. The paucity of wallrock alteration adjacent to the Puzzle vein indicates that endothermic alteration reactions could not have cooled the fluids appreciably. Initial studies of deuterium:hydrogen ratios in fluid inclusions in sphalerite from the OH vein at Creede by Roedder (1967, p. 555) indicates that the inclusion fluids are significantly different in this ratio than local groundwater and it can be concluded that significant mixing of hypogene fluids and groundwater did not occur. It should be stressed that deuterium-hydrogen studies are relatively new and if past experience with older isotopic tools is repeated, the results of the deuterium-hydrogen studies will be reinterpreted and revised as more experience is attained. There is no conclusive available evidence on the degree to which groundwater mixing can be used as a mechanism for cooling the hypogene fluids which formed the Puzzle vein.

One of the most promising mechanisms for cooling hydrothermal fluids is irreversible adiabatic expansion or throttling. The process involves expansion of a fluid at constant enthalpy upon passing from a region
of higher pressure to one of lower pressure. Meeves and Darnell (1968, p. 23 and 24) describe the results of deep exploration on the Amethyst vein at elevations of approximately 8900, 9050 and 9075 feet. The deep exploration was below the productive portion of the Amethyst vein and the Amethyst fault was found to consist of only a few inches of gouge accompanied by a mud and boulder filling. It is suggested that throttling occurred at depth in the Puzzle vein in a similar geologic environment where the structure changes from a narrow fault zone below to an open fissure above; the inferred locus of throttling is below the presently exposed portion of the vein.

The deposition of the Puzzle vein is conceived to have occurred in response to cooling of an ascending ore-forming fluid. The cooling probably involved a combination of the mechanisms described above and possibly additional unrecognized mechanisms. The most likely and important mechanisms are adjudged to be throttling and groundwater mixing.

In summary the Puzzle vein formed in the epithermal temperature range under a total pressure of approximately 50-150 bars at a depth of 1100-2100 feet beneath the existing land surface.

It is not possible to give a quantitative statement of the pH of the hypogene fluid or fluids. Because of the paucity of alteration in the rhyolitic wallrock of the vein it is inferred that the fluid or fluids were not appreciably acid. The pre-volcanic basement under the Creede district contains carbonate rocks which would tend to neutralize any ascending fluid which was initially acid. Similarly the silicic nature of the volcanic wallrock would tend to neutralize a hydrothermal fluid which was initially basic (Krauskopf, 1967, p. 495). It is concluded that the fluid or fluids that formed the Puzzle vein were near
neutrality during the final stages of transport and during vein mineral deposition although the pH was probably not seven due to the increase in the dissociation constant of water at temperatures up to 230 degrees Celsius. The depositional processes varied regarding equilibrium from at or near equilibrium between the fluid and solid phases near the bottom of the deposit as presently exposed to marked disequilibrium near the top of the vein. The change in equilibrium conditions reflects the presence of a supersaturation gradient with increasing supersaturation towards the top of the vein.

The mobilization, transfer and emplacement of metals to form the Puzzle vein effected a manifold concentration relative to average crustal abundances. The grade of the ore in the Puzzle vein has been calculated to be approximately 3.2 percent lead and 21.4 troy ounces of silver per ton. The average crustal abundances of lead and silver have been estimated to be 12.5 and 0.07 ppm respectively (Krauskopf, 1967, p. 639 and 640). Thus the mineralizing process has concentrated lead in the ore about 2,400 times in relation to crustal abundance. Silver has been concentrated approximately 10,300 times.

Roedder (1965, p. 381) has utilized a vacuum crushing technique to analyze primary fluid inclusions in sphalerite from the OH vein at Creede. His analyses show the following atomic ratios: K/Na - 0.11, Ca/Na - 0.22, Mg/Na - 0.027, Cl/Na - 1.53, B/Na - 0.02, SO$_4$/Na - 0.02 and Ca/Mg - 8. The presence of the sulfate ion in primary fluid inclusions from Creede may be significant in terms of the nature of sulfur transport in hydrothermal fluids. It should be recalled that the sulfur isotope data presented above were interpreted to mean that transport of sulfate from a sedimentary evaporite or connate brine source was at least
a permissible mechanism to explain the sulfur isotope composition of the Puzzle vein. The fluid inclusions in the sphalerite from the OH vein contain vapor bubbles as well as liquid but no solid phases, suggesting that the ore-forming fluid was not saturated with NaCl at the time of vein deposition. Neutron activation analysis of the primary inclusion fluid in quartz from an unspecified locality in the Creede district reveals that the fluid contains 140, 690 and 1,330 ppm of copper, manganese and zinc respectively (Roedder, 1965, p. 380).

It is concluded that the hydrothermal fluid, which formed the Puzzle vein, was most likely a dense, hot saline brine with a pH near or at neutrality. Vein mineral deposition resulted from increasing supersaturation as the ascending fluid cooled due to throttling and mixing with groundwater.

Classification

The indirect reasoning presented above indicates that the temperature of formation of the exposed upper part of the Puzzle vein is in the epithermal range of 50-200 degrees Celsius proposed by Lindgren (1933, p. 212). The texture and mineralogy of the Puzzle vein support an epithermal classification based upon the probable temperature of formation. The temperature may well have been near the upper end of the epithermal range and the Puzzle vein at depth may cross the epithermal-mesothermal boundary. Graton (1933, p. 537) proposed the use of the term leptothermal for deposits which formed at or near the boundary between Lindgren's epithermal and mesothermal categories. One of Graton's type examples was the Camp Bird vein in the San Juan Mountains which has textural and mineralogical similarities to the Puzzle vein. There are many differences between the Puzzle and Camp Bird veins, however, and Graton did not define
temperature limits for his leptothermal category. The Puzzle vein could be classified as either epithermal or leptothermal and it may pass into a more typically mesothermal vein at greater depth.

ENVIRONMENT OF OXIDATION AND SUPERGENE DEPOSITION

Extent of oxidation in the Puzzle vein

The Puzzle vein is only slightly oxidized over most of its lateral and vertical extent. Thorough oxidation of sulfide minerals is seen at only a few localities. Some slight oxidation effects are seen at the deepest part of the Bulldog Mountain mine. The mine is unusually dry and there is little groundwater moving through the vein at present. Massive pyrite in places on the 9700 level is untarnished even where the botryoidal surface of original deposition projects into an open fissure. Minerals characteristic of supergene environments such as covellite and chalcocite are seen only in a few polished sections and are nowhere abundant. It has not been possible to map a spatially distinct zone of supergene enrichment and enrichment is believed to be minor, from both geologic and economic standpoints. It is possible that a more distinct zone of supergene enrichment will be found below the 9360 level but the paucity of oxidation in the upper part of the vein precludes any substantial supergene enrichment at depth. The relation of native silver to supergene and hypogene processes is discussed below in a separate section.

Oxidation and supergene enrichment probably began as soon as hypogene deposition ceased and it has continued on a minor scale until the present time. The temperature during the oxidation of the vein is not known although ambient temperatures probably prevailed as there is no evidence
that substantial exothermic oxidation of sulfide minerals has occurred.

Nature of the supergene fluid

The composition of the supergene fluid can be ascertained in only a general way. Supergene minerals include sulfates (goslarite and chalcanthite), a carbonate (cerussite), a chloride (mimetite), oxides (cuprite and goethite), native elements (silver and copper) and a molybdate (wulfenite). Illite, kaolinite, montmorillonite, nontronite and alunite may all be supergene in origin. Chalcocite, covellite, acanthite, bornite, calcite and hematite may also be of supergene origin.

It is not possible to obtain an uncontaminated sample of mine water from the Bulldog Mountain mine because the mine utilizes a sand backfill system in the stopes which uses mill tailings, and surface water is used for drilling. Emmons and Larsen (1923, p. 128 and 129) reported the results of water analyses from the Amethyst and Solomon-Holy Moses veins. These waters were described as alkaline and carry sulfate and carbon dioxide (Emmons and Larsen, op. cit.). The results of the analyses are tabulated below in Table 10. The analyses from the Amethyst and Solomon-Holy Moses veins are compatible with the supergene mineral suite in the Puzzle vein. The water analyses from the older mines are used to estimate anion abundances for the purpose of making redox calculations as discussed below.

Eh-pH in the supergene environment

The minerals of the oxidation zone and their sulfide precursors are plotted on a redox diagram in an attempt to define the Eh and pH environment during oxidation and supergene alteration of the Puzzle vein (figure 30). Any calculation of Eh-pH stability fields involves several fundamental and critical assumptions. For present purposes standard
Figure 30 Eh-pH diagram of the supergene environment in the Puzzle vein at 25°C and 1 atmosphere. Shaded area encompasses the probable Eh and pH limits.
TABLE 10  ANALYSES OF MINE WATERS FROM CREED, COLORADO
(after Emmons and Larsen, 1923, p. 128)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>28.52</td>
<td>7.5</td>
</tr>
<tr>
<td>K</td>
<td>2.41</td>
<td>3.5</td>
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<tr>
<td>Ca</td>
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<td>46.2</td>
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<td>Mg</td>
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<tr>
<td>S0_4</td>
<td>60.12</td>
<td>104.4</td>
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<tr>
<td>Cl^-</td>
<td>trace</td>
<td>1.6</td>
</tr>
<tr>
<td>HCO_3</td>
<td>62.83</td>
<td>71.8</td>
</tr>
<tr>
<td>Fe_2O_3 - Al_2O_3</td>
<td>2.10</td>
<td>1.2</td>
</tr>
<tr>
<td>SiO_2</td>
<td>32.35</td>
<td>23.2</td>
</tr>
</tbody>
</table>

All analyses reported in ppm

1 - Amethyst vein, Bachelor mine
2 - Solomon-Holy Moses vein, Solomon mine

temperature and pressure of 25 degrees Celsius and one atmosphere are assumed. Copper, lead and silver are assumed to be present in concentrations of 10^-5 molar in the ionic state although the effect of changing the silver concentration to lower levels is examined. Molybdenum is assigned a concentration of 10^-6 molar in accord with Hansuld (1966, p. 75) as no hypogene molybdenum minerals were identified in the vein. It should be noted that a concentration of 10^-5 molar is approximately equal to one part per million. The concentration of the sulfate and carbonate ions is assumed to be 10^-3 molar.

The stability fields of the lead minerals anglesite, cerussite, wulfenite and galena are plotted using the method of Krauskopf (1967, p. 519). The reactions chosen for the lead minerals are given below.

\[
PbS0_4 \rightleftharpoons Pb^{++} + SO_4^-
\]

\[
PbCO_3 \rightleftharpoons Pb^{++} + CO_3^-
\]

\[
PbS \rightleftharpoons Pb^{++} + S^-
\]

\[
PbMoO_4 \rightleftharpoons Pb^{++} + MoO_4^-
\]

The absence of anglesite in the oxide zone of the Puzzle vein indicates that the pH was high, a conclusion in accord with the observed paucity of pyrite oxidation.
The presence of minor supergene native silver, as discussed below in the section on native silver genesis, allows a further narrowing of the boundaries of the possible Eh—pH environment. The assumed reaction for silver is given below.

$$\text{Ag} \rightleftharpoons \text{Ag}^+ + e^-$$

The Ag—Ag⁺ boundary is independent of pH in the range of pH values encountered in geologic environments and this boundary can safely be extended across the diagram as a horizontal line. The Ag—Ag⁺ boundary is very sensitive to the concentration of silver ion in the supergene fluid. There are no useful available data on the expected silver content of descending waters in the Creede district. A concentration of $10^{-5}$ molar or about one ppm is probably the maximum which can be reasonably expected. The boundaries for $10^{-7}$ and $10^{-9}$ molar concentrations of silver ion are plotted (figure 30).

At a few localities in intensely oxidized portions of the vein, supergene native silver coexists with native copper and cuprite. The equation is $2\text{Cu} + \text{OH}^- \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e^-$ is used to calculate the boundary between cuprite and native copper. The redox diagram would indicate that the stability field of coexisting cuprite and native copper lies within the stability fields of both native silver and cerussite. The reaction to form cuprite is suspect because of the notorious slowness of redox reactions involving oxygen-bearing species and cuprite could be metastable in the supergene environment of the Puzzle vein. The cuprite—native copper boundary could be adjusted considerably and still be within the stability fields for both cerussite and native silver. The absence of tenorite in the oxidation zone of the Puzzle vein places an upper
limit on the Eh of the environment at varying pH in the neutral to alkaline range. The equation \( \text{Cu} + 2\text{OH}^- \rightleftharpoons \text{CuO} + \text{H}_2\text{O} + 2\text{e}^- \) is used to establish the tenorite-native copper boundary.

Because of inherent uncertainties in the assumptions noted above and in the precise nature of the reactions it would be dangerous to attempt to narrow the Eh-pH environment further. This discussion has assumed that the redox conditions were uniform throughout the zone of oxidation whereas in reality there has probably been a variation in these conditions.

The absence of anglesite and the presence of cuprite and wulfenite indicate a pH near or greater than neutrality. The limits of pH are considered to be in the range of 5.7 to 9.3 and the limits of Eh are in the range of -0.10 to +0.2 depending upon pH. These Eh and pH limits are shown by the shaded area in Figure 30.

The alkaline supergene environment which has been reconstructed for the Puzzle vein is evidence against widespread native silver genesis by supergene processes. Many previous workers including Emmons (1917, p. 263) and Boyle (1968, p. 191) have noted that silver mobility in the supergene environment is enhanced at low pH but retarded at high pH. The presence of unoxidized pyrite throughout the Puzzle vein supports the conclusion that alkaline conditions have prevailed during oxidation of the Puzzle vein. The alkaline environment has been of considerable importance as it has prevented the remobilization of the hypogene native silver which makes the Puzzle vein an economic asset.
ORIGIN OF NATIVE SILVER IN THE PUZZLE VEIN

The origin of the native silver in the Puzzle vein is of particular interest due to the dominant economic importance of this mineral and because the distribution of the native silver can be expected to reflect the operation of both hypogene and supergene processes in the vein.

Previous geologic studies of the Creede district have resulted in the conclusion that the high concentration of native silver was due to downward enrichment (Emmons and Larsen, 1923, p. 98, 116 and 117, and Steven and Ratté, 1965, p. 77). The Puzzle vein presents an opportunity to study the distribution and origin of native silver in a blind vein which has undergone only local oxidation. It should be stressed that the veins exposed to previous workers in the district crop out and are much more intensely oxidized. The conclusions presented herein regarding native silver genesis apply to only the Puzzle vein.

The occurrence and distribution of native silver in the Puzzle vein is pertinent to any discussion of genesis. The bulk of the native silver is found at sites throughout the mine which show little or no evidence of oxidation. The megascopic native silver at these sites occurs as either irregular clusters of wires resembling steel wool or at a few sites as massive veinlets as much as two inches wide. The veinlets are considered to represent open spaces which have completely filled with wire silver. Microscopic examination reveals the presence of native silver along fractures and grain boundaries in all of the earlier minerals. There is no preferred association of the microscopic native silver with any particular mineral. The wire silver contains microscopic inclusions of galena, sphalerite and chalcopyrite and tarnishes black in situ.
A small amount of the native silver occurs as flakes or spangles associated with native copper, cuprite and limonitic jasper in a few obviously oxidized localities on the 9700 level where sulfide minerals are absent. The spangles of native silver are untarnished in situ and contain no inclusions of hypogene minerals.

A supergene origin for the native silver in the Puzzle vein can be established only if a source of silver in hypogene minerals is identified and if the amount of silver in the hypogene source minerals is adequate to account for the amount of native silver in the vein. Both of these requirements are evaluated in the following paragraph.

The Puzzle vein pinches upwards as it passes into less competent wallrock. The vertical interval available for oxidation, leaching and supergene enrichment is certainly less than the estimated 1,600 ± 500 feet thickness of cover at the time of deposition. The vein does not reach the present surface where the East strand of the Bulldog Mountain fault is exposed. Therefore the maximum vertical interval available for leaching lies between the 10,800 feet maximum elevation of the projected outcrop of the vein and the approximate 9,800 feet elevation of the top of ore in the vein. Thus the maximum interval which could conceivably have been leached is approximately 1,000 feet measured vertically or about 1,100 feet if measured in the plane of the vein. Any hypothesis which invokes a supergene origin for the native silver in the Puzzle vein must, of necessity, derive the supergene silver from a maximum vertical interval of 1,000 feet.

Trace analyses of the vein minerals have shown that only galena has an appreciable silver content and galena is the only mineral present in sufficient abundance to furnish silver for supergene enrichment. The
maximum silver content of the galena is less than 200 ppm as shown by the electron microprobe analysis and confirmed by atomic absorption analysis. The lead content of the ore shoots in the Puzzle vein is 3.2 percent and the ratio of the lead content of galena to the lead content of the ore is 28.85:1. Oxidation of vein material averaging the same as the presently exposed ore could thus contribute a maximum of only about 200/28.85 ppm or about 0.21 troy ounces of silver per ton to supergene fluids. The presently exposed ore bodies have a vertical range of about 400 feet and the silver content in this interval is 21.4 troy ounces per ton (1968, Homestake Mining Company annual report). If it is assumed that the vein, which was leached to provide supergene silver, had the same thickness and strike length as the vein which is exposed and if the galena content was uniform throughout, then the required vertical interval for leaching can be calculated. Using 21.0/0.21 as the ratio of the silver content of the present ore bodies contributed by native silver to the silver content contributed by galena, the calculated requisite vertical interval of leaching is approximately 40,000 feet. The hypothetical vertical interval of 40,000 feet is a conservative minimum as it assumes that the vein does not decrease in width upwards and that the efficiency of oxidation, leaching and supergene deposition was 100 percent. Both of these assumptions are unreasonable as the vein narrows upwards and it is highly unlikely that supergene processes are ever 100 percent efficient.

The efficiency of oxidation is of particular interest, as there are analytical data which shed light on this process in the Puzzle vein. During the month of September, 1969, which is the only month for which relatively complete data are available, the oxide lead content of the ore from the Bulldog Mountain mine ranged from 1.15 to 7.50 percent of the
total lead content. The remainder was sulfide lead. This range disregards a single oxide lead assay of 36.45 percent of the total lead, which is considered to be spurious and represent an error in either assaying or reporting of assay results. It is not possible to calculate a true monthly average of the oxide lead content because the data would have to be weighted for tonnage which is not available and no grade data are available for three days of the month. A simple arithmetic mean for the month, eliminating the single high sample, is 2.68 percent oxide lead, i.e., oxide lead is 2.68 percent of the total lead content of the vein. It is readily apparent that oxidation and leaching of the portion of the Puzzle vein being mined during the month of September, 1969 cannot be used as a mechanism to derive silver for supergene enrichment to form appreciable native silver. The data for this particular month are believed to be representative of the exposed portion of the Puzzle vein. Thus oxidation and leaching of the interval of the vein between the 9700 and 9360 levels cannot be used as a source of silver to support a supergene origin for the bulk of the native silver. The native silver in the Puzzle vein can reasonably be expected to persist below the 9360 level. Any extension of the native silver to greater depth extends the interval required for leaching if the silver genesis is to be explained by supergene processes.

The possibility of the prior presence of hypogene silver-bearing minerals in the hypothetical leached zone, which are not present in the exposed vein, cannot be ruled out but is considered very unlikely. In this regard it should be recalled that abundant silver-bearing minerals, other than native silver, have not been described in previous studies of the Creede district. It is possible that the native silver could have
formed by in situ alteration of a hypogene silver-bearing mineral, e.g., by alteration of acanthite. Such a process would need to have been nearly 100 percent efficient as there is little acanthite in the Puzzle vein as exposed to date. It is illogical to suppose that any such process was 100 percent effective in altering a pre-existing silver mineral to native silver.

It is concluded that the wire silver which forms the bulk of the native silver in the Puzzle vein is hypogene in origin. The relatively minor spangles of silver are believed to be of supergene origin.

SOURCE OF THE ORE-FORMING COMPONENTS

The lead and sulfur isotope data, when integrated with the geologic environment, indicate a complex genesis of the ore-forming fluid or fluids. The lead and sulfur were each derived from at least two sources, although not necessarily the same two sources for each.

The lead isotope data indicate that lead genesis was at least a two stage process beginning with evolution in a deep source region which is generally considered to be the earth's mantle. The deep source region is required to explain the evolution of lead isotopes in a region of homogeneous uranium and thorium composition as the geochemical environment in the oxygen rich crust of the earth results in fractionation of thorium and uranium and their separation. The history of the lead now found in galena in the Puzzle vein includes transfer from the deep source region and emplacement in the crust in Precambrian time. The subsequent history of the lead is less certain. The lead from the Precambrian environment may have been re-emplaced in a Jurassic or Cretaceous host rock during the Laramide orogeny or alternatively the lead may have been retained in
the Precambrian host until remobilization concurrent with the Oligocene volcanism. In either case the lead from the Precambrian environment was contaminated with radiogenic lead prior to final emplacement in the Puzzle vein. The radiogenic lead was derived from an environment with a low thorium:uranium ratio. The most likely source of the radiogenic lead is a carbonate or evaporite sedimentary rock of Jurassic or Cretaceous age. Only a precipitate sedimentary rock has the requisite low thorium:uranium ratio.

The sulfur isotope data indicate that a portion of the sulfur in the Puzzle vein was derived from a deep primordial source. The zero permil value for the sulfide minerals cannot logically be explained by isotopic fractionation of sulfur from a single source in view of the preponderance of barite in the vein. The deep source of some of the sulfur is either the mantle or the lower crust. Additional sulfur is believed to be derived through remobilization of sulfate sulfur in a sedimentary source rock.

Erosion along the Uncompahgre-San Luis highland removed all post-Precambrian and pre-Jurassic strata from the central San Juan Mountains. The formation of the Puzzle vein is part of a larger regional process of volcanism which affected the rocks in the San Juan region. The most likely source of the radiogenic lead and sedimentary sulfate is the sedimentary section of Jurassic and Cretaceous age. As noted above in the section on regional geology, an evaporite facies is found in the Todilto Limestone of Jurassic age. This evaporite unit is an obvious source of the sulfate sulfur. Alternatively the sulfate sulfur could have been derived from connate brines elsewhere within the Mesozoic stratigraphic section. The radiogenic lead could have come from the same source as the sulfate sulfur or from a completely different source in the Mesozoic section. It is noteworthy that the oxygen and carbon isotope study of Steven and Friedman (1968, p. B33) on travertine in the Creede
Formation resulted in a similar conclusion to those given above for some of the lead and sulfur. Steven and Friedman preferred a sedimentary carbonate source in the Mesozoic column for the oxygen and carbon in the travertine.

The source of the vein forming components, other than lead and sulfur, is not known. It is likely that the metals such as zinc, silver, and copper were derived partly from the lower crust or mantle and partly from the sedimentary section traversed by the ore-forming fluid or fluids. Similarly it is probable that the abundant ions found in the fluid inclusions of the Creede district, such as sodium and chloride, have multiple sources.

The source of the hydrothermal fluid cannot be ascertained but it is likely that the aqueous component was derived from both juvenile and connate sources. Some mixing of the hypogene fluid and meteoric water at or near the site of vein formation is probable.

RELATION OF THE ORE FORMATION TO VOLCANISM

The formation of the Puzzle vein is part of a larger geologic process of volcanism which affected the entire San Juan region. The close association of volcanic activity and ore genesis in both time and space at Creede necessitates a re-examination of the source of the volcanic rocks. Lead and strontium isotope studies on volcanic rocks from the Creede area indicate that the parent magma was derived from a deep source in either the lower crust or mantle (Doe, 1968, p. 149). The isotope data rule out remelting of Precambrian rocks as a source of the Oligocene volcanic rocks (Doe, 1968, p. 170). The lead isotopes in galena are slightly more radiogenic than the lead isotopes in the volcanic host rocks and
it is tentatively concluded by Doe (op. cit.) and by the writer that all of the lead in the ore was not derived from the same source as the parental magma of the volcanic rocks. The magma responsible for the volcanic rocks may have acted as an energy source to mobilize the metals and sulfur which formed the Puzzle vein.

Ore deposition followed the cessation of volcanic activity very closely in time. The youngest pre-ore volcanic formation at Creede has been dated at $26.4 \pm 0.6$ million years as noted above in the section on geology of the Creede mining district. The early stage of vein formation in the OH vein at Creede has been dated at about 26 million years (Bethke, P., 1968, written communication). The major ore deposits at Creede, including the Puzzle vein, are localized in fault structures which are a direct product of stresses related to the ascent and withdrawal of the parent magma of the volcanic rocks. The deposition of the Puzzle vein is intimately related to a sequence of events which began with the eruption of ash flow tuffs and was followed successively by caldera collapse, additional eruption, resurgent doming of the caldera, renewed eruption, faulting, and finally hydrothermal vein deposition. Minor faulting and dike intrusion followed vein formation.
EPILOG

Here's a land where all are equal
of high or lowly birth

A land where men make millions
dug from the dreary earth

Here the meek and mild eyed burros
on mineral mountains feed

It's day all day in the day-time
and there is no night in Creede

The cliffs are solid silver
with wondrous wealth untold

And the beds of running rivers
are lined with glittering gold

While the world is filled with sorrows
and hearts must break and bleed

It's day all day in the day-time
and there is no night in Creede

Cy Warman
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APPENDIX A ATOMIC ABSORPTION ANALYSES FOR SILVER

All of the common hypogene sulfide minerals were analyzed by atomic absorption spectrography to study the distribution of silver in the Puzzle vein. Samples of each mineral were separated by hand picking and by using the Franz isodynamic separator model LI. The digestion procedure is listed below.

1. Add 1 gram of KCIO₃ as an oxidizing agent to 1 gram of the sample to the analyzed.
2. Wet with 1N HNO₃.
3. Add 15-20 ml. concentrated HNO₃.
4. Heat to dissolve and take to dryness.
5. Redissolve with 20-25 ml. 6N HNO₃.
6. Heat to insure complete dissolution, filter and wash container with hot distilled water.
7. Dilute to 100 ml. volume for stock solution of the unknown.
8. Make further dilutions as required for instrumental analysis.

Fresh standards were prepared on the day of the analysis by dissolving silver foil in 6N HNO₃. The silver foil was heated to remove admixed oxidation products prior to weighing.

Analyses were performed on a Perkin-Elmer Model 303 atomic absorption spectrometer utilizing either digital concentration readout or a strip chart recorder. Detection limits for silver in solution are 0.5 and 0.1 ppm for the digital and recorder readouts respectively. The instrument was operated with an air-acetylene flame using an aspiration rate of approximately 20 seconds per milliliter. Final values for the silver were obtained from three replicate analyses per sample when using...
the recorder or five replicate analyses per sample with the digital readout.

APPENDIX B ELECTRON MICROPROBE ANALYSIS

Various compositional aspects of vein minerals were examined with a Material Analysis Company Model 400 electron microprobe. Polished sections of the minerals were coated with either a graphite or a platinum-palladium overcoating to insure conductivity of the surface. The electron beam was operated at 15 kilovolts and 0.01-0.02 microamps. Instrument design parameters include an angle of incidence of 62.5 degrees and a takeoff angle of 33.5 degrees. Detection limits ranged from 0.4 percent for gold and 0.1 percent for mercury to 0.03 percent for lead and zinc.

APPENDIX C MERCURY ANALYSIS

The common hypogene sulfide minerals, barite and the two textural varieties of native silver were analyzed for mercury with a Lemaire Instruments Company Model SI mercury detector. The analyses were performed on 1.0 and 0.1 gram samples. Detection limits are approximately 0.04 and 0.4 ppm for the larger and smaller samples respectively.

The instrument was operated with a heating interval of 1.5 minutes per sample. Stainless steel pumps were utilized with a new fiberglass filter for each sample. Each sample bulb was purged of any residual mercury content by heating prior to use. Care was taken to insure that sulfur from the sulfide minerals did not interfere with the results.
APPENDIX D  LEAD ISOTOPE ANALYSIS

Lead isotope analyses of galena samples were performed by Isotopes of Westwood, New Jersey using a 12 inch, 60 degree mass spectrometer. The galena samples were initially dissolved in 10 ml. of 1:1 HNO₃ and 1 ml. of HClO₄. After digestion the residue was taken into solution with 2N HCl, the pH adjusted to approximately 3 with dilute NH₄OH and the lead precipitated with H₂S gas. The precipitate was redissolved in HNO₃ and reprecipitated as the nitrate on a tungsten filament.

APPENDIX E  SULFUR ISOTOPE ANALYSIS

Sulfur isotope analyses were performed in the isotope geology laboratory at the University of Utah through the courtesy of Dr. M. L. Jensen. Details of the analytical techniques are given in Jensen, 1967, p. 145 and 146.