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Geology and geochemistry of the Bully Hill area of the East Shasta district, Shasta County, California

Gustin, Michael McComb, Ph.D.

The University of Arizona, 1989
GEOLOGY AND GEOCHEMISTRY OF THE BULLY HILL AREA
OF THE EAST SHASTA DISTRICT,
SHASTA COUNTY, CALIFORNIA

by
Michael McComb Gustin

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF GEOSCIENCES
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1990
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Michael McComb Gustin entitled Geology and Geochemistry of the Bully Hill Area of the East Shasta District, Shasta County, California

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

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ABSTRACT

Late Permian kuroko-type mineralization in the Bully Hill area of the East Shasta district formed along two horizons within the Bully Hill rhyolite. In the Bully Hill, Rising Star, and Copper City mine areas, syngenetic mineralization is underlain by alteration zones characterized by addition of SiO₂ and K₂O, loss of Na₂O, CaO, and Fe₂O₃, and the assemblage quartz + sericite + pyrite. Quartz precipitation in the upper portion of the zones led to cyclic sealing of fluid flow, rupturing of the seal, quartz supersaturation, focused fluid discharge, and formation of sulfide mounds on the seafloor.

Syngenetic mineralization occurred in several Stages: (1) deposition of fine-grained banded sulfides and gangue; (2a) recrystallization of Stage 1 minerals, and void-filling by pyrite + weakly chalcopyrite-diseased sphalerite ± barite; (2b) deposition of coarsely-crystalline pyrite + heavily chalcopyrite-diseased sphalerite; (3a) void-filling and replacement by galena + chalcopyrite + tetrahedrite-tennantite; (3b) replacement by chalcopyrite; and (4) replacement by barite. ΣSO₄ and H₂S contents of hydrothermal fluids decreased from Stages 2a to 3a. δ³⁴S values of sulfides increased successively from Stages 1 (-15.8 per mil) to 3a (3.0 per mil), reflecting variable
inputs of biogenic sulfur and deep-seated fluid evolution.  
\( \delta^{34}\text{S} \) values of syngenetic barites range from 12.4 to 22.5 per mil, reflecting cold seawater and hydrothermal sulfur sources, respectively.

\( \delta^{34}\text{S} \) values of epigenetic pyrite and barite within the alteration zones range from -0.7 to 2.7 per mil and 12.4 to 24.1 per mil, respectively. Primary and pseudosecondary fluid inclusions in epigenetic minerals have filling temperatures of 240 to 260°C and salinities of 3 to 12.3 equivalent weight percent NaCl.

Lower limits of fluid salinities and \( \delta^{34}\text{S} \) values of barite indicate that seawater was a primary component of the hydrothermal fluid, and that seawater also mixed with discharging fluids on the seafloor. High fluid salinities, the lack of a silica source, and the close link of magmatism with mineralization indicate that magmatic fluids may have been an important component of the hydrothermal fluids.
CHAPTER 1

INTRODUCTION

Scope of This Study

The purpose of this study was to reevaluate the geology and geochemistry of the Bully Hill portion of the East Shasta massive sulfide district in Shasta County, California. This work was undertaken as part of a larger effort at the University of Arizona which encompasses the entire district.

The most comprehensive work on the district was completed by Albers and Robertson (1961). They concluded that the ore bodies of the district are epigenetic replacement deposits formed along shear zones in volcanic and sedimentary rocks. They believed that the mineralizing event took place much later than the deposition of the host rocks.

In the late 1960's and early 1970's, many massive sulfide deposits similar to the East Shasta ores were reinterpreted to be volcanogenic deposits (e.g., Anderson, 1969). Although the East Shasta ores have been widely reclassified as volcanogenic massive sulfide deposits (e.g., Hutchinson, 1973; Meyer, 1981) detailed geologic documentation of the deposits in the district has only been presented
for the mineralization in the area of the Afterthought mine (Fredericks, 1980; Eastoe and Nelson, 1988).

For this study, the principal areas of mineralization in the Bully Hill portion of the East Shasta district were mapped at various levels of detail in order to provide a geologic base for geochemical interpretations. Samples of the Bully Hill rhyolite, which hosts the deposits, the Dekkas andesite, and examples of the various styles of mineralization were examined petrographically. Geochemical results, including whole rock, sulfur isotope, and fluid inclusion analyses, are combined with these data in order to present a geological and geochemical model of the ore-forming processes.

Location

The East Shasta district is located in Shasta County, California, in the southeastern corner of the Klamath Mountains geologic province. The district is centered on two main areas of mineralization: the Afterthought mine area in the southeastern portion of the district and the Bully Hill area, which is the subject of this study. The study area, which will be referred to as the Bully Hill area, lies along the northern shore of the Squaw Creek arm of Shasta Lake in the north-central portion of the East Shasta district, as defined by Albers and Robertson (1961), approximately 27 kilometers northeast of
Redding, California (Figure 1). The area includes portions of Sections 9, 10, 11, 14, 15, 16, 17, 20, 21, 22, 28, 29, 30 and 31, T 34 N, R 3 W, MDM, on the Bollibokka Mountain (1:62500) quadrangle map.

The Bully Hill area includes the Bully Hill and Rising Star mines, on the slopes of Bully Hill, the Copper City mine, approximately 2 kilometers southwest of Bully Hill, and the Shasta May Blossom prospect, about 2.5 kilometers east of Bully Hill (Figure 2). Bully Hill, located in the southeast quarter of Section 16, is a prominent positive topographic feature among the generally low-lying foothills of Horse and Town Mountains.

The study area may be reached from Redding by 19 kilometers of paved road to Jones Valley and then by boat 8 kilometers across Shasta Lake. Alternatively, there are two overland routes to the project area consisting of long dirt roads which connect with U.S. 299E and Interstate Highway 5, as shown on county maps. These dirt roads range from well to poorly maintained. The overland routes from Redding to Bully Hill are approximately 100 kilometers long. Unmaintained dirt roads and variably overgrown foot paths provide partial access within the generally densely vegetated study area.
Figure 1. Location of study area. BH = Bully Hill; Aft = Afterthought mine
Figure 2. Simplified geologic map of the Bully Hill area, adapted from Albers and Robertson (1961), showing sample locations, areas of detailed study, and the Rising Star, Bully Hill-Copper City and Shasta May Blossom mineralized horizons. See Figure 21 for sample locations in the Bully Hill-Rising Star mine area. Map areas: A = Bully Hill-Rising Star; B = Copper City; C = Shasta May Blossom.
Mining History

The following is an abbreviated summary of the history of mining in the Bully Hill area taken largely from the more extensive review by Albers and Robertson (1961).

The discovery of placer gold in the early 1850's in Town Creek along the eastern slopes of Bully Hill and in many of the gullies draining Bully Hill marked the beginning of mining activity in the East Shasta district. The resultant interest in the presence of placer gold led to the discovery in 1862 of gold and silver in gossans outcropping at what became the Copper City and Bully Hill mines. Gold and silver were mined from the gossans intermittently from 1862 to 1899 from shallow pits and adits. In 1877, the Extra Mining Co. built the first mill in the area at Copper City and during the next four years the mill produced a reported $640,000 in gold and silver. When secondary sulfide ores immediately below the gossans were encountered the mill was no longer effective in extracting the precious metals.

Interest in high-grade secondarily enriched copper mineralization below the gossans led to the construction of a 150 ton capacity blast furnace by J. R. Delamar and the development of the Bully Hill mine on a large scale in 1901. By 1902, the ore being mined at Bully Hill had high zinc contents that caused metallurgical problems; this led to the development of the Rising Star mine. In 1908, the smelter
was remodeled and its capacity was increased to 800 tons per day in order to keep pace with the 1000 ton per day hoisting capacity at the Rising Star and Bully Hill mines. The years from 1901 to 1910 were the boom years for copper, gold, and silver mining at Bully Hill.

In 1910, the smelter and mines at Bully Hill closed, probably because of high zinc to copper ratios in the ores, which would have caused direct smelting methods to be unpractical. Smelter damage to nearby crops and forests may also have played a role in the closure. From 1915 to 1927, several attempts at developing an economic extraction process for the zinc-rich ores met with varying success, and minor amounts of copper, zinc, and precious metals were recovered. No metal has been produced from the Bully Hill area since 1927.

In 1944 the Shasta Dam was completed and the water in the newly created Shasta Lake flooded the lower workings of the Copper City mine. All other underground workings in the Bully Hill area are also presently inaccessible because of caving and closure of the portals.

In the period from 1900 to 1927, the Bully Hill and Rising Star mines combined to produce about 580,000 tons of ore containing 49 million pounds of copper, 2.2 million ounces of silver and 38,000 ounces of gold. From 1913 to 1927 approximately 25 million pounds of zinc were produced; prior to this time no zinc could be recovered and it was
lost in mine waste. The Copper City mine was never an important producer; the only known production consisted of 250 tons of high-grade copper, gold, and silver ore (Albers and Robertson, 1961). No ore was produced at the Shasta May Blossom prospect. The production at the Bully Hill and Rising Star mines represents about 78% of the total tonnage mined in the East Shasta district to date.

Previous Work

The first geologic publication to include a discussion of the Bully Hill area was a report on the geology and mineralogy of Shasta County by Fairbanks (1893). A year later, Smith (1894) reported on the stratigraphy and paleontology of the area adjacent to the McCloud and Pit Rivers. In a report on metamorphic rocks west of Shasta County, Hershey (1901) briefly mentioned rocks which occur in the Bully Hill area.

In the early 1900's, Diller published a series of reports on the geology of the Klamath Mountains. Included in these are a review of the sedimentary stratigraphy and paleontology of the Klamath Mountains, with a brief mention of the area in the vicinity of the confluence of the Pit River and Squaw Creek (Diller, 1903a); a survey of the geology of the copper deposits of the Redding quadrangle, including the Bully Hill district (Diller, 1903b); an update on mining activities in the Redding quadrangle, which in-
cluded a brief description of the geology of the Rising Star and Bully Hill mines (Diller, 1904); and the excellent geologic map, cross-sections, description of stratigraphy and review of the ore deposits of the Redding quadrangle published in the Redding Folio (Diller, 1906). The Redding Folio is a classic geologic work that has only been refined by later studies.

Aubury (1908), in a review of copper deposits of California, discussed the status of mining properties in the vicinity of Bully Hill and presented a history of mining in the district. A more detailed investigation of the geology and ore deposits of the Bully Hill area than Diller's earlier work was undertaken by Graton (1910). Further description of the geology of the mines and prospects in the Bully Hill area was published by Brown (1916).

Other papers that include references to the geology of the area include reports by Hinds (1932) on the Paleozoic igneous rocks of the southern Klamath Mountains; Hinds (1933) on the stratigraphy of the Weaverville and Redding quadrangles; Hinds (1935) on the Mesozoic and Cenozoic "eruptive" rocks of the southern Klamath Mountains; and Hinds (1940) on the Paleozoic section of the southern Klamath Mountains.

In 1961 Albers and Robertson published a detailed report on the geology and ore deposits of the East Shasta district. The report includes a geologic map and detailed
descriptive text. This work has been the basis of all subsequent study in the district.

More recent literature on the East Shasta district includes reports containing Pb isotopic data on ores of both the East and West Shasta districts by Doe and Zartman (1979) and Slawson (1983), a thesis on the volcanic lithofacies of the Afterthought mine area of the East Shasta district (Fredericks, 1980), a paper documenting the presence of sedimentary clasts of sulfides in rocks stratigraphically above massive sulfide mineralization in both the East and West Shasta districts (Watkins and Stensrud, 1983), a thesis on a previously unmapped portion of the district to the west of the Afterthought mine area (Nelson, 1986) and a study of the geology and mineralization of the Afterthought mine area (Eastoe and Nelson, 1988). The geochemistry, petrology and tectonic setting of the Nosoni Formation, Dekkas andesite, and Bully Hill rhyolite have been presented in a series of recent papers (Lapierre et al., 1986; Martin, Lapierre, and Coulon, 1985; Martin, Lapierre and Rocci, 1984; and Lapierre, Albers, and Martin, 1983). Eastoe, Gustin, and Nelson (1987) reported on the presence of an olistostrome deposit exposed throughout the East Shasta district in the lower Pit Formation.
Field and Laboratory Methods

Field work was undertaken in the summers of 1983 and 1985. A 1:4800 scale aerial photograph was used as a map base for the geologic mapping of the Bully Hill-Rising Star and Copper City mine areas. No attempt was made to correct for possible distortions in the photos. The Shasta May Blossom prospect and regional geology were mapped on the U.S.G.S. Bollibokka Mountain 15' topographic map at a photographically-increased scale of 1:24000. The geologic map and descriptive text of Albers and Robertson (1961) were used as a geologic base for all field work and subsequent geologic interpretations.

All underground workings in the Bully Hill area were inaccessible at the time of the field work. Mine and prospect dumps were therefore used extensively for petrographic and geochemical sampling in order to attain relatively unweathered samples of mineralized rocks. Drill core of Northair Mines Ltd. was also briefly inspected, but not sampled.

Whole rocks were analyzed by x-ray fluorescence by X-Ray Assay Laboratories Limited (XRAL) of Don Mills, Ontario, and TerraMin Research Labs Ltd. (TML) of Vancouver, British Columbia. Fused pellets were used for all elements except Y, Nb, and Zr, for which pressed powder pellets were utilized. The detection limit for major elements is 0.01%, with 10 ppm for Ba, 3 ppm for Zr, and 2 ppm for Y and Nb.
Fluid inclusion heating and freezing determinations were performed at the University of Arizona on a U.S.G.S.-S.G.E. gas-flow heating-freezing stage. Chromel-alumel and iron-constantan thermocouples were used with a Doric 400A Trendicator digital temperature indicator, which has a resolution of 0.1°C. The thermocouples were calibrated using Pennsylvania State University pure H₂O standards for 0.0°C and critical point temperature determinations and pure CO₂ for calibration at the triple point. A Leitz metronic microscope with 16x oculars and long-focal-length condenser was used for fluid inclusion thermometry. A 50x long-focal-length universal stage objective provided the maximum magnification of the microscope. This objective has an effective magnification of approximately 32x when used without the universal hemispheric stage.

Pyrite, barite, and anhydrite separates for sulfur isotopic analysis were sorted by hand, panned, or both. H₂S from the sphalerite + galena fraction of complex massive sulfide ore was liberated through digestion in boiling dilute HCl and reprecipitated as PbS after introduction into a solution of lead nitrate. SO₂ was derived from sulfides by reaction with Cu₂O at 950°C (Robinson and Kusakabe, 1975) and from sulfates by reaction with Cu₂O and SiO₂ at 1,100°C (Coleman and Moore, 1978). The SO₂ gas was purified and subsequently analyzed at the University of Arizona by a modified Micromass 602 mass spectrometer. Calibrations were
achieved by mutual comparison of National Bureau of Stan-
dards 123 (17.2 per mil) and five laboratory standards (-8
to +17 per mil) from the University of Arizona and the
University of Tasmania. The Tasmanian laboratory standards
were tested against standards of the Department of
Scientific Industrial Research (New Zealand), Bureau of
Mineral Resources (Australia), and the Ontario Geological
Survey.

An automated ARL electron microprobe with computer-
linked software for data reduction was used in wavelength
dispersive mode to determine the composition of sphalerites.
An accelerating voltage of 15kv, a sample current of 30
nanoamperes, and a beam diameter of 10 microns were used.
Intensity data were reduced to concentrations using the
method of Bence and Albee (1969). Energy dispersive mode
was used to identify several mineral species.
CHAPTER 2

REGIONAL GEOLOGY

Klamath Mountains Geologic Province

The Klamath Mountains geologic province of southwestern Oregon and northwestern California is bound to the north and west by the Coast Ranges province, and is overlapped to the east and south by the Cascade volcanic province and sediments of the Great Valley Sequence, respectively. It consists predominantly of Paleozoic and Mesozoic island arc-related volcanic and sedimentary rocks, ophiolitic sequences, and isolated ultramafic bodies of uncertain origin (Irwin, 1981). Plutons, largely of Jurassic and Cretaceous ages (Hotz, 1971), intrude many portions of the province.

The Klamath Mountains province has been subdivided into four fault-bounded tectonostratigraphic terranes named, from west to east, the western Jurassic terrane, the western Paleozoic and Triassic terrane, the central metamorphic terrane and the eastern Klamath terrane (Irwin, 1981; Irwin, 1966; Figure 3). The western Paleozoic and Triassic terrane is further subdivided into the Rattlesnake Creek, Hayfork and North Fork terranes. Strata of the eastern Klamath terrane have been less formally subdivided into the Yreka-
Figure 3. Terrane map of the Klamath Mountains province, adapted from Irwin (1981).
Callahan area in the north and the Redding section to the south (Irwin, 1981). The Middle Ordovician Trinity ultramafic sheet (Lanphere, Irwin, and Hotz, 1968) is exposed between these and forms the basement of the eastern Klamath terrane (Irwin, 1981; Griscom, 1977).

The entire sequence of terranes forms an imbricate gently east-dipping structural section. The geologic framework of the province is thought to be the result of the sequential tectonic accretion of remnants of oceanic crust and island arcs to the western margin of North America in the Jurassic (Hamilton, 1969; Irwin, 1981; Lapierre et al., 1986).

**Redding Section Stratigraphy**

The East Shasta district is located within the Redding section of the eastern Klamath terrane (Figure 3). The Redding section includes arc-related volcanic and sedimentary rocks representative of all of the systems from Devonian through Middle Jurassic (Irwin, 1981). These rocks form a grossly conformable east-dipping homoclinal section with an exposed stratigraphic thickness of more than 10 to as much as 15 kilometers (Irwin, 1977). In a regional sense the Redding section is only moderately deformed and of low metamorphic grade (Lapierre et al, 1986; Reed, 1984; Barker, Millard, and Knight, 1979; Albers and Robertson, 1961).
Two major accumulations of felsic volcanic rocks occur within the Redding section, the Devonian Balaklala rhyolite and the Permian Bully Hill rhyolite. These formations host the massive sulfide mineralization of the West Shasta (Kinkel et al., 1956) and East Shasta districts, respectively.

In the vicinity of the East Shasta district, rocks of the Redding section are unconformably overlain by Plio-Pleistocene volcanic rocks of the Cascade province. These include predominantly andesitic to basaltic flows and pyroclastic deposits (Albers and Robertson, 1961).

**Overview of the Geology of the East Shasta District**

The mineralization of the East Shasta district is hosted by a Permian island arc sequence which has been subdivided into the Nosoni formation, the Dekkas andesite and the Bully Hill rhyolite. These volcanic rocks were deposited on the McCloud limestone and are overlain by sediments of the Pit formation (Table 1).

The McCloud limestone is a fossiliferous limestone containing fusulinid assemblages that indicate an Early Permian age (Albers and Robertson, 1961). The contact between the McCloud and the volcanic rocks has recently been reinterpreted as conformable (Lapierre et al., 1983; Roure, 1984).
Table 1. Stratigraphy of the Bully Hill Area.

<table>
<thead>
<tr>
<th>Age</th>
<th>Formation</th>
<th>Thickness (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle</td>
<td>Pit Formation</td>
<td>600-1350 (1)</td>
</tr>
<tr>
<td>TRIASSIC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early</td>
<td>Bully Hill Rhyolite</td>
<td>50-750 (1)</td>
</tr>
<tr>
<td>Late</td>
<td>Dekkas Andesite</td>
<td>300-1100 (1)</td>
</tr>
<tr>
<td></td>
<td>Nosoni Formation</td>
<td>0-1000 (1,2)</td>
</tr>
<tr>
<td>PERMIAN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early</td>
<td>McCloud Limestone</td>
<td>0-800 (3,4)</td>
</tr>
</tbody>
</table>

References: (1) Albers and Robertson (1961), (2) Lapierre et al. (1986), (3) Skinner and Wilde (1969) and (4) Watkins (1986)
The Nosoni formation is composed of basalt, dacite, andesite, and rhyolite lavas and associated pyroclastic deposits interlayered with mudstones (Lapierre et al., 1986). Sparse carbonate rocks containing fusulinids of Early to Late Permian age also occur (Lapierre et al., 1983). Several mafic-to-felsic cycles are present within the Nosoni volcanic rocks (Martin, personal communication to Eastoe, 1987).

The Dekkas andesite conformably overlies the Nosoni formation (Albers and Robertson, 1961). Within the East Shasta area, the Dekkas andesite consists predominantly of andesitic to basaltic flows, breccias, and tuffs interbedded with minor fine-grained siliceous sediments. To the north of the East Shasta district, the Dekkas andesite contains abundant water-lain pyroclastics and, toward the top, basaltic lava and discontinuous lenses of shallow-water limestone (Miller, 1989). Late Permian fossils occur in the lower part of the Dekkas andesite (Albers and Robertson, 1961), and a late Permian fossil assemblage which includes fauna of both Tethyan and North American affinities occurs at the top of the formation in the northeastern portion of the Redding section.

The Bully Hill rhyolite, which hosts the bulk of the mineralization of the East Shasta district, conformably overlies the Dekkas andesite (Albers and Robertson, 1961). It represents a thin deposit of felsic volcanic material
overlying the relatively thick andesitic accumulation of the Dekkas andesite. The Bully Hill rhyolite is composed chiefly of aphanitic to feldspar-phyric dacitic lavas and quartz+feldspar-phyric rhyodacitic to rhyolitic flows, flow breccias, and pyroclastic deposits. In the Bully Hill area dacitic units are most common at the base of the formation, with quartz-phyric units predominating higher in the section. Andesitic to basaltic lavas, intrusions, tuffs and volcanogenic sediments occur sporadically at the top of the formation and comprise what is informally referred to in this paper as the upper mafic unit of the Bully Hill rhyolite. Similar mafic volcanic rocks within the Bully Hill rhyolite overlie the felsic rocks west of the Afterthought mine (Eastoe and Nelson, 1988).

The Dekkas andesite and Bully Hill rhyolite appear to represent a single mafic-to-felsic cycle. Mafic volcanic rocks occur locally near the top of the Bully Hill rhyolite and at the base of the Pit formation. Late Permian radiolarians found in chert at the base of the Pit formation immediately above the Bully Hill rhyolite indicate that the Dekkas and Bully Hill formations in the Bully Hill area are entirely of Late Permian age (Silberling and Jones, 1982).

Felsic lithologies similar to those of the Bully Hill rhyolite are also found interbedded in both the Dekkas and Pit formations, in many cases making the limits of the Bully Hill rhyolite difficult to define. Where this occurs
Albers and Robertson (1961) defined the lower contact of the Bully Hill rhyolite at the point where felsic rocks predominate over more mafic lithologies typical of the Dekkas andesite, and the lower contact of the Pit formation at the stratigraphically lowest occurrence of shale or mudstone typical of the main mass of the Pit.

Exposures of the Bully Hill rhyolite are confined to the East Shasta district, where it outcrops primarily in two areas. The exposure in the southeastern portion of the district is host to mineralization of the Afterthought mine and adjacent prospects. The lenticular mass of Bully Hill rhyolite exposed in the northern portion of the district, referred to in this paper as the Bully Hill area, hosts the mineralization of the Bully Hill, Rising Star, Copper City and Shasta May Blossom mines. Each of these occurrences of Bully Hill rhyolite may represent accumulations from separate vents (Albers and Robertson, 1961).

The Pit formation conformably overlies all units of the volcanic terrane (Albers and Robertson, 1961). The bulk of the Pit formation consists of fine-grained sediments, including mudstone, shale, siltstone and argillite, and interbedded intermediate to felsic pyroclastic deposits. The volcanic component is more prevalent in the lower portion of the formation. In the East Shasta area the base of the Pit formation appears to be a large olistostromal deposit (Eastoe et al., 1987). The age of the bulk of the Pit
formation at Hawkins Creek, located approximately 35 kilometers northeast of the field area is Middle Triassic (Curtis, 1983).

The Permo-Triassic rocks exposed in the East Shasta district were affected by a low grade of metamorphism. Curtis (1983) defined a quartz-prehnite zone in the lower 500 meters and a zone of laumontite subfacies of the zeolite facies above 500 meters in the Pit formation at Hawkins Creek. Lapierre et al. (1986) recognized zeolite and prehnite facies metamorphic assemblages within the Nosoni and Dekkas volcanic rocks.

The base and precious metal mineralization of the East Shasta district occurs primarily as isolated or clustered lenses of massive sulfide. These sulfide bodies occur predominantly at the contact of the Bully Hill rhyolite and the Pit formation, and within the Bully Hill rhyolite close to this contact. A few lenses occur within the Pit formation (Albers and Robertson, 1961). Exploitation of the massive sulfide ores has been centered about the Afterthought mine area near the ghost town of Ingot, and at Bully Hill.

On the basis of geochemical and lithological characteristics of the Nosoni, Dekkas and Bully Hill formations, Lapierre et al. (1986) suggested that these rocks were deposited in a mature island arc environment which formed near the North American continental margin in the late
Permian. The arc was built upon the McCloud limestone carbonate platform. The volcanic rocks are of the low-K tholeiitic series, and differentiation was the major process in their genesis (Lapierre et al., 1986). This arc was accreted to North America in the Jurassic (Hamilton, 1969; Irwin, 1981; Lapierre et al., 1986).
CHAPTER 3

STRATIGRAPHY AND ALTERATION OF THE BULLY HILL AREA

Introduction

The three principal areas of mineralization in the Bully Hill area -- the Bully Hill-Rising Star, Copper City and Shasta May Blossom mine areas -- were investigated in various degrees of detail. Much of the region underlain by the Bully Hill rhyolite between these mineralized areas and portions of the Dekkas andesite were also examined in reconnaissance fashion, in order to build a geologic framework for the entire Bully Hill area.

Dekkas Andesite

In the Bully Hill area the Dekkas andesite consists primarily of andesitic massive to autobrecciated lava and lithic-rich pyroclastic deposits, with minor intercalated lenses of mudstone. Volcanic rocks of basaltic composition are less common.

Several thin-sections of the Dekkas andesite from the section stratigraphically below Bully Hill were examined. The volcanic rocks are extensively hydrothermally altered, with titanomagnetite the sole primary igneous phase recognized.
The lavas, as seen in both massive flows and as lithic fragments in pyroclastic rocks, consist of plagioclase phenocrysts and microlites in an intersertal groundmass. Pilotaxitic texture and amygdules are common. The plagioclase phenocrysts commonly have albite twinning and optically continuous rims of plagioclase, and may occur in clusters. Petrographic evidence suggests that the igneous plagioclase has been extensively replaced by albite; microprobe analyses indicate albite contents of 97 to 98 mole percent in both the core and rim of a phenocryst which was analyzed. Sparse relict pyroxene phenocrysts are pseudomorphed by secondary minerals, and often contain subophitic to ophitic albite microlites.

The secondary mineral assemblage in volcanic rocks of the Dekkas andesite consists of chlorite, albite, iron oxides, calcite, epidote, pumpellyite, sphene, leucoxene, pyrite, quartz, sericite, prehnite and barite, in approximate order of decreasing volumetric abundance. Paragenetic relationships in veinlets, amygdules and alteration of igneous phases and groundmass are consistent and suggest an alteration sequence of (1) chlorite, (2) calcite with or without quartz, (3) chlorite, (4) epidote and pumpellyite with or without prehnite, (5) iron oxide, and (6) chlorite. Albitization of the feldspars probably preceded all of these stages. Hexagonal flakes of hematite may accompany any of the chlorite stages. Pyrite occurs disseminated in the
groundmass and as an alteration product of feldspar and pyroxene, and is paragenetically earlier than pumpellyite. Sericite and other clay minerals are minor alteration products of feldspar, and barite is an uncommon phase in amygdules.

Iron oxide alteration of the Dekkas andesite appears to be especially prevalent near the contact of the Dekkas andesite and Bully Hill rhyolite. In this area, iron oxides pervasively replace the groundmass, leaving albite phenocrysts and microlites as unreplaced islands within masses of iron oxide and creating a breccia texture. In some cases the iron oxide replacement can be seen to pervade outward from amygdules and irregular veinlets into the groundmass.

A pre-depositional (primary) phase of hematitization is evidenced by andesitic pyroclastic rocks in which some lithic fragments are extensively hematitized and others are not. Miller (1989) reported similar hematitic lithic fragments within Dekkas pyroclastic rocks near Lake McCloud (approximately 40 kilometers north-northeast of Bully Hill). Miller (1979) reported that green chloritic volcanic rocks predominate in the lower portion of the Dekkas andesite, while red hematitic volcanic rocks and fossiliferous shallow water limestone are common towards the top of the formation. She concluded that the Dekkas section at Lake McCloud represents a more distal facies of a stratocone than those in the
East Shasta district, with the vertical lithologic changes indicating upward shoaling.

**Bully Hill-Rising Star Mine Area**

**Rock Units**

Workings and prospects associated with the Bully Hill and Rising Star mines are located on the eastern and southern flanks of Bully Hill, respectively, entirely within the Bully Hill rhyolite near its contact with the overlying Pit formation. Within the Bully Hill-Rising Star mine area the Bully Hill rhyolite is subdivided into four units, informally named the lower tuff, lava, tuff breccia and upper tuff units (Figures 4 and 5). These units are overlain by various lithologies of the lower Pit formation. The upper portion of the Bully Hill rhyolite and the lowermost Pit formation are intruded by mafic sills.

**Lower Tuff Unit (bt₁).** The lowermost unit of the Bully Hill rhyolite overlies andesitic pyroclastic deposits of the Dekkas andesite. The lower tuff unit consists of various quartz-phyric lithic tuffs, ranging from beds of well-sorted, finely-layered coarse ash tuffs to lentils of poorly-sorted agglomeritic deposits with fragments up to a meter or more in the longest dimension. Rhyodacitic quartz crystal lithic tuff breccia is the predominant rock type of the lower tuff unit. Minor dacitic to rhyolitic flows and flow-breccias are also present. Fragments within the tuffs
EXPLANATION

PIT FORMATION

BULLY HILL RHYOLITE
Upper tuff unit
Tuff breccia unit
Lava unit
Lower tuff unit

DEKKAS ANDESITE
Strike and dip
bedding
flow banding
schistosity
space cleavage

Geologic contact, dashed where inferred
Fault, dashed where inferred
Shear zone, showing dip
Axial trace of anticline
Overturned anticline
Shaft
dirt road
mine dump

Figure 4. Geology of the Bully Hill-Rising Star mine area. Explanation is on page 46; map on page 47. Map base: aerial photograph.
Figure 4, continued.
Figure 5. Geologic cross-section of the Bully Hill-Rising Star mine area. Horizontal = vertical scale. Geologic symbols same as in Figure 4.
are predominantly subangular to subrounded coarse lapilli-sized pieces of flow-banded quartz-phyric rhyodacitic lava. Exotic rounded fragments of quartz monzonite(?), consisting of quartz, plagioclase and biotite, up to 0.5 meters in diameter occur with fragments of flow-banded felsic lava in an irregular bed of agglomerate in the middle of the unit (bt\(_1\)a). The source of this plutonic rock is unknown. The coarse-grained lithic tuffs of bt\(_1\) are clast-supported.

The well-developed bedding in the fine-grained tuffaceous rocks of the lower tuff unit suggests deposition in a subaqueous environment. The rounding of the fragments in the coarse lithic tuff breccias and agglomerates and clast-supported nature suggests that these represent reworked pyroclastic deposits (talus breccias).

Fragmental rocks exposed in the core of the anticline on Bully Hill are interpreted to be part of the lower tuff unit. These rocks include clast-supported crystal lithic tuffs, lithic crystal lapilli tuffs, and rhyodacitic flows and flow-breccias, all of which contain quartz phenocrysts. Lithic fragments within the pyroclastic rocks consist predominantly of quartz-phyric flow-banded lava.

**Lava Unit (bl).** A series of generally highly-altered quartz-phyric rhyodacitic to rhyolitic lava flows and flow-breccias overlies the lower tuff unit. In unaltered exposures, which occur primarily beyond the limits of the map area, the groundmass of the lava is typically greenish-
grey to greyish-black, and plagioclase phenocrysts are also present. Flow-banding is common in both the massive and autobrecciated lavas. Flow-breccia fragments are angular to subrounded, less than one meter in the longest dimension, are commonly flow-banded and are of the same composition as the matrix lava.

Phenocryst abundance in the lavas ranges from 5 to 20 volume percent, with plagioclase predominating over quartz phenocrysts. The phenocrysts are up to 5 mm in diameter. In the least-altered rocks the former presence of sparse ferromagnesian phenocrysts is locally evidenced by patches of chlorite, epidote-clinozoisite, pyrite, apatite and leucoxene.

Quartz phenocrysts typically have equant, rounded shapes and are commonly embayed; euhedral (locally dipyramidal) forms also occur. Feldspar phenocrysts are predominantly subhedral to euhedral, have poorly- to well-developed albite and Carlsbad twinning and commonly occur in clusters. Petrographic evidence suggests that the plagioclase is albite, with compositions ranging from $\text{Ab}_{90-100}$ (Albers and Robertson, 1961). The phenocrysts are locally fractured and slightly brecciated.

The groundmass of the lava is aphanitic, consisting of anhedral microcrystalline quartz and subordinate plagioclase microlites. Chlorite occurs as a minor interstitial phase, and probably partially replaced the originally glassy
matrix. Minor amounts of epidote, pyrite and sericite with or without calcite and iron-rich carbonate are disseminated throughout the groundmass. Microspherulitic texture is present locally; relict perlitic texture was observed in one slightly altered sample. Zircon is present as a trace, accessory phase.

Lenses of tuffaceous rocks (blt), including clast-supported lithic tuff breccia similar to rocks of the tuff breccia unit (below) and minor thinly-bedded fine-grained volcaniclastic rocks, also occur within the lava unit. Only a few of these lenses are shown on Figure 4. Examination of Northair Mines Ltd. drill core from the Bully Hill mine area suggests that the tuffaceous lithologies within the lava unit are more prevalent than is obvious from surface exposures.

Two subunits, not delineated on Figure 4, can be defined within the lava unit. The lower subunit is composed predominantly of autobrecciated lava, and its extent is largely coincident with the limits of the Type 1 alteration zone associated with the Rising Star mine (Figure 6; see below). The upper subunit is dominated by flow-banded lavas, and is capped by the autobrecciated lavas characteristic of the Type 1 alteration zone of the Bully Hill mine.

The presence of thinly-bedded volcaniclastic rocks within the lava unit suggests that it was deposited suba-
Figure 6. Map showing distribution of alteration types in the Bully Hill-Rising Star mine area. Type 6 alteration occurs stratigraphically above the alteration types shown, in the hangingwall of the Bully Hill horizon (see text).
queously. The abundant autobrecciated flows may also pro-
vide evidence of subaqueous extrusion of the silicic lavas
(de Rosen-Spence et al., 1980).

**Tuff Breccia Unit (bt₂).** In the west and southwest
portion of the map area the lava unit is overlain by a
fairly uniform unit of quartz ± plagioclase crystal lithic
coarse lapilli tuff breccia. The tuff breccias are poorly-
sorted, and locally exhibit crude bedding. A thin mudstone
bed was observed within the tuffs at one locality.

The tuff breccia is similar to the coarse lapilli
tuffs of the lower tuff unit. The tuffs are clast-support-
ed, and fragments are predominantly subrounded, consist
chiefly of quartz-phyric rhyodacite, and are up to 0.5
meters in the longest dimension. Andesitic to dacitic
lithic fragments and less commonly fragments of semi-massive
fine-grained pyrite also occur. In areas where the unit as
a whole is unaltered, silicified and sericitized felsic
fragments and chloritized andesitic fragments are present.
This suggests that the fragments were altered prior to
incorporation into the tuff.

To the southeast the tuff breccia unit is inter-
bedded with flows of the uppermost portion of the lava unit.
Tuffaceous rocks identical to those in the tuff breccia unit
occur sporadically near the top of the lava unit throughout
the map area and are interpreted to be correlative. Similar
tuffs in the upper portion of the lava unit have been inter-
sected by Northair Mines Ltd. in diamond drill holes in the Bully Hill mine area.

The rounded fragments, bedded nature and presence of interbedded mudstone in the tuff breccia unit are evidence that it was deposited subaqueously. The rounded fragments, bedding and clast-supported framework also suggest that this unit was deposited as talus breccias deposited during submarine slumping events.

**Upper Tuff Unit (bt₃).** The uppermost unit of the Bully Hill rhyolite in the Bully Hill-Rising Star mine area is lithologically heterogeneous and poorly exposed. The unit is largely unsilicified, in marked contrast to all of the underlying units. The predominant lithology is quartz + plagioclase crystal lithic lapilli tuff. Crystal tuffs and lithic crystal tuffs also occur. In the southwesternmost portion of Figure 4, a thinly-bedded well-sorted crystal lithic fine lapilli tuff or tuffaceous sediment is exposed at the base of the upper tuff unit along the mine road (bt₃t).

Where exposure is adequate, bedding is commonly discernible within the upper tuff unit. The tuff is usually deeply weathered, with a red-orange or less commonly purple color. Much of this tuff is identical to the felsic orange tuffs characteristic of the lower Pit formation.

In the southeastern portion of the map area the upper unit includes breccias apparently formed by slumping.
Breccia fragments are up to a few tens of centimeters in the longest dimension and consist of angular, variably silicified fragments of quartz and feldspar-phyric flow-banded lava supported by an unsilicified, clayey and chloritic matrix. These breccias are exposed in cuts of the Rising Star mine access road. Several outcrops of unaltered flow-banded quartz, feldspar and hornblende(?)-phyric lava occur about one hundred meters to the south of the road cuts. These small outcrops of lava may be transported blocks within the slump breccia.

**Pit Formation (p).** The lowermost Pit formation exposed in the Bully Hill-Rising Star mine area consists of andesitic tuffs and minor intercalated beds of mudstone. These are overlain by interbedded mudstone and red-orange deeply-weathered felsic tuff (Plates 8 and 11, Albers and Robertson, 1961). Isolated outcrops of relatively unaltered quartz and plagioclase-phyric dacite also occur within the Pit formation in this area.

Lithologic complexity and chaotic orientations of bedding and minor fold axes characterize the lower Pit formation in the Bully Hill-Rising Star mine area (Plate 8, Albers and Robertson, 1961; Figure 4), in contrast to the lithologic and structural uniformity of the remainder of the overlying Pit formation (Plate 1, Albers and Robertson, 1961). Similar chaotic styles are found in the lowermost Pit formation on the shores of Shasta Lake near the Copper
City mine, where more extensive exposure has led to the interpretation that the lower Pit formation is an olistostromal megabreccia (Eastoe et al., 1987).

Mafic Intrusions. Amygdaloidal mafic sills intrude the lowermost portion of the Pit formation, the upper tuff unit and the lava unit (Plate 8, Albers and Robertson, 1961). These intrusions are too small to be shown on Figure 4. The majority of the sills intrude the upper tuff unit close to its contact with the underlying lava unit. In surface exposures and Northair's drill core the sills are unaltered, in marked contrast to the rocks they intrude, although Albers and Robertson (1961) reported that some of the sills are altered and sheared in underground exposures.

The sills are largely aphanitic. Where they are porphyritic, clusters of plagioclase phenocrysts up to 5 mm in diameter occur in a groundmass of abundant felty plagioclase microlites and interstitial chlorite, which appears to replace glass. Minor epidote is also present in the groundmass. Calcite and quartz are the most common amygdule phases (Albers and Robertson, 1961). In one specimen, amygdules are composed of barite and two distinct phases of chlorite, with filling textures suggesting that barite is later than both chlorite types.

The presence of barite as an amygdule-filling phase and the local silicification of the sills suggest that
intrusion occurred late in the life of the hydrothermal system at Bully Hill.

**Limonitic Gossan.** Numerous small gossanous bodies, not identified on Figure 4, occur within the map area. These consist of masses of limonite cementing locally-derived rock fragments. The limonite bodies all occur within or downslope from faults and sheared contacts within mineralized areas. The limonite is interpreted to be predominantly exotic.

**Hydrothermal Alteration**

Six generalized megascopic hydrothermal alteration facies (Types 1 through 6, below) have been defined in the Bully Hill-Rising Star map area (Figure 6). The facies are named sequentially according to overall degree of alteration, with Type 1 representing the most extreme alteration facies. A seventh facies is assigned to the relatively unaltered rocks which occur immediately beyond the map area.

In this document, fine-grained colorless mica with moderately-high birefringence is called sericite. Albers and Robertson (1961) determined that this mineral is hydrous mica, based on its indices of refraction and a single microprobe analysis.

**Type 1.** Type 1 alteration zones occur entirely within the lava unit and outcrop as resistant, craggy north to north-northeast-trending ribs which control the topo-
graphic expression of Bully Hill (Figure 7). Autobrecciated lava is the predominant lithologic component of these ridges (Figure 8).

Type 1 alteration consists in essentially complete replacement of the protolith by fine-grained quartz, with quartz phenocrysts and accessory zircon the only surviving igneous phases. Plagioclase phenocrysts are replaced entirely by xenomorphic quartz ± sericite. Quartz phenocrysts are rimmed by irregular, optically-continuous overgrowths. The groundmass consists of anhedral microcrystalline quartz and generally less than 10 volume percent sericite. Disseminated pyrite is present in varying percentages. Irregular relatively coarse-grained areas of quartz flooding of the matrix record fluid paths along flow foliations. Discrete quartz veinlets may also parallel primary foliations in the lavas. Iron-rich carbonate is an important alteration phase in one sample of Type 1 alteration.

Type 1 alteration is characteristically accompanied by stockwork mineralization of white quartz, quartz + pyrite ± chalcopyrite and barite ± pyrite ± quartz veinlets. The stockwork mineralization cross-cuts the intense silicification and disseminated pyrite mineralization. Quartz flooding along quartz veinlet selvages is common, and represents a second stage of silicification. Grey-colored quartz + sulfide veinlets are the earliest of the three stockwork veinlet types. White quartz veinlets cross-cut and fill
Figure 7. Rising Star Type 1 alteration zone forming ridge on south slope of Bully Hill.
voids within the gray quartz + sulfide veinlets. Both types of quartz veinlets are commonly highly contorted and irregular.

Barite occurs as irregular veinlets and pods which crosscut and partially replace the quartz veinlets (Figure 9). This epigenetic barite is subdivided into grey and white types. Grey barite smells strongly of \( \text{H}_2\text{S} \) gas when a crystal is freshly broken, contains abundant fluid inclusions, is commonly associated with macroscopic and/or microscopic sulfide minerals, and is essentially restricted to Type 1 alteration zones. White barite emits no \( \text{H}_2\text{S} \) odor, contains sparse fluid inclusions, is rarely associated with any sulfides and occurs in both Types 1 and 2 alteration zones. No paragenetic relationships between grey and white barite veinlets were observed.

Extensional gash-filling milky quartz veinlets and veins, locally common in Type 1 alteration zones, crosscut all of the stockwork vein types.

At the Bully Hill mine Type 1 alteration is exposed discontinuously along and immediately below the contact of the lava and upper tuff units. At the Rising Star mine Type 1 alteration overlaps with the updip projection of the stoped ore bodies (compare Figures 4 and 11). Type 1 alteration is therefore interpreted to occupy semi-conformable zones in the immediate stratigraphic footwall of the massive sulfide horizons. The stockwork mineralization is inter-
Figure 8. Close-up of ridge of Type 1 alteration of Figure 7 showing autobreciated lava of lava unit.
interpreted to have acted in part as feeder channels to the overlying sulfide accumulations. The faulted extensions of the folded Rising Star mine horizons can be traced to the north by the linear, north-trending exposures of Type 1 alteration (Figure 4).

**Type 2.** Type 2 alteration is more extensive and laterally continuous than Type 1 alteration. It occurs within the lava unit and the discontinuous portions of the tuff breccia unit contained within it. Although generally well-exposed, rocks exhibiting Type 2 alteration do not form the resistant ridges characteristic of Type 1 zones.

Type 2 alteration is similar to Type 1 in all respects except that sericite is a more abundant alteration phase and the stockwork mineralization occurs only locally. Sericite generally makes up 20 to 40 volume percent of the groundmass, and occurs as sparse microveinlets. Alunite occurs as fine-grained subhedral crystals intermixed with quartz and sericite in the matrix of one thin-section.

**Type 3.** Type 3 alteration is characterized by less intense silicification and more prevalent sericitization than Type 2. Rocks within this facies are usually more deeply weathered and are not as well exposed as rocks exhibiting Types 1 and 2 alteration.

Although no igneous plagioclase occurs within this facies, relict albite twinning in replaced phenocrysts can locally be detected. Plagioclase phenocrysts are replaced
by variable amounts of quartz and sericite; calcite is a locally abundant alteration product of the feldspar. Relict plagioclase microlites, replaced by quartz, are present in some thin-sections. The groundmass consists of anhedral quartz, typically 30 to 60 volume percent sericite and rare chlorite. Relict ferromagnesian phenocrysts pseudomorphed by quartz, chlorite, apatite, pyrite and leucoxene are rarely present.

Areas of Type 3 alteration lie stratigraphically below and laterally beyond the areas of Types 1 and 2 alteration, which are more proximal to the ore horizons of the Bully Hill and Rising Star mines. Type 3 grades into relatively unaltered rocks in the western and northern portions of the map area, and is most intensely developed immediately below Type 1 and 2 alteration zones.

Type 4. Type 4 alteration occurs at the base of the lower tuff unit of the Bully Hill rhyolite. Alteration minerals include albite, quartz, chlorite, sericite, calcite and pyrite. Chlorite contents in the matrix of the lithic tuffs range from 10 to 30 volume percent. Plagioclase fragments are partially to completely replaced by the secondary minerals.

Type 5. Type 5 alteration is specific to much of the tuff breccia unit. Silicification, as represented by microcrystalline replacement quartz in the matrix, is variable but less intensely developed than in the alteration
Figure 9. Stockwork grey barite mineralization within Type 1 alteration zone.

Figure 10. Blocks of contorted mudstone in tuffaceous matrix (orange tuff) in lower Pit formation 800 m northeast of trench at the Copper City mine.
Figure 11. Surface projection of stopes of the Bully Hill and Rising Star mines, from Plate 10 of Albers and Robertson (1961). Numbers indicate level of stopes; levels are at approximately 100 foot intervals. Rising Star Mine: level 1 = 1469 feet above sea level, level 8 = 747 feet; Bully Hill mine: level 1 = 1610 feet, level 11 = 607 feet.
types discussed previously. Sericite is a minor alteration phase. Calcite is a common alteration product of the matrix, plagioclase fragments and lithic fragments. Chlorite is an alteration phase of variable abundance. Albite replaces plagioclase crystal fragments.

Alteration intensity within the tuff breccia unit in the southwestern portion of the map area increases towards its contact with the underlying lava unit. Flow-breccia blocks of the lava unit at this contact are often selectively silicified, chloritized, and sericitized. Pyrite contents in both units also increase in this area.

**Type 6.** Type 6 alteration is quite distinct from the alteration types discussed to this point in that it does not include significant silicification. Plagioclase phenocrysts are relatively unaltered. This zone occurs in the upper tuff unit and lower Pit formation, lying stratigraphically above the previous alteration types. Since these rocks are so highly weathered, it could not be determined to what extent the alteration assemblage reflects a hypogene hydrothermal assemblage. Minerals characteristic of this alteration type include sericite, chlorite, clay minerals and quartz. Pyrite is present locally. Rocks of this zone are locally moderately silicified at the contact with the underlying lava unit.

**Type 7.** Alteration Types 3, 4, 5 and 6 grade into relatively unaltered rocks, generally immediately beyond the
limits of Figure 4. Although appearing fresh in hand samples, these rocks are actually altered with respect to pristine volcanic rocks. This weak alteration facies is Type 7 alteration, and it is found regionally in the Bully Hill area.

The characteristic mineral assemblage of Type 7 alteration is quartz, albite, chlorite, epidote-clinozoisite, pyrite, sericite and leucoxene with or without kaolinite, calcite and iron-rich carbonate. Albite phenocrysts are fresh to weakly altered, silicification is weak and restricted to groundmass replacement with or without quartz phenocryst overgrowths, and sericite contents are generally well below 10 volume percent. Relict ferromagnesian minerals are pseudomorphed by chlorite, epidote, apatite, pyrite and leucoxene with or without carbonate.

Copper City Mine Area

The Copper City mine is located on the north shore of Shasta Lake approximately 2 kilometers southwest of Bully Hill (Figure 2). The many workings and prospects are located on the flanks of Kilanger Peak, which forms a slight positive topographic anomaly.

Rock Units and Hydrothermal Alteration

The geology of the Copper City mine area was investigated in less detail than the Bully Hill-Rising Star
mine area. Figure 12 shows the geology of the Copper City area.

In the Copper City area, the Bully Hill rhyolite is exposed in the core of a north-trending anticline and consists of highly silicified dacitic lavas, tuffs and volcaniclastic rocks with rare quartz phenocrysts. Quartz ± sulfide and barite veinlets occur locally.

The upper contact of the Bully Hill rhyolite is marked by the presence of resistant ribs of Type 1 alteration and its associated mineralization, as defined in the discussion of the Bully Hill-Rising Star mine area. These ribs are composed predominantly of intensely silicified breccias and massive to autobrecciated quartz phenocryst-poor dacitic lava. The breccias are made up of angular fragments of mudstone and the dacitic lava.

Surface projections of stopes within the Copper City underground workings (Plate 14, Albers and Robertson, 1961) and the distribution of surface prospects (Figure 12) strongly support the interpretation that the Type 1 alteration zones are genetically related to and stratigraphically below the horizon which contains the massive sulfide deposits developed to date. The full extent of the Type 1 alteration zone therefore defines the mineralized horizon of the Copper City area.

The area west of the trench at the Copper City mine is underlain by volcaniclastic rocks of the Bully Hill
Figure 12. Geologic map of the Copper City mine area. bhr = Bully Hill rhyolite; other symbols are the same as in Figure 4. Map base: aerial photograph.
rhyolite. Lithologies range from fine-grained thinly-bedded tuffaceous sediments to conglomeratic deposits. Some clasts were silicified prior to incorporation into the deposits. One outcrop consists entirely of pebble-sized clasts of coarsely crystalline barite, and a small lens of fragmental, reworked massive sulfide is exposed in the trench. Bedding attitudes in the volcaniclastic rocks are not consistent with the local structure, and may be overturned. These characteristics suggest that the volcaniclastic rocks are slump deposits. Isolated outcrops of Type 1 altered lava(?) occur at the contact of the unit with the overlying Pit formation, and may be transported blocks.

When low lake levels afforded essentially complete exposure along the shoreline at Copper City in the summer of 1985, the lower Pit formation was seen to be composed of tabular, often isoclinally folded, blocks of mudstone, siltstone and shale set within a massive tuffaceous matrix (orange tuff) (Figure 10). The orange-weathering tuffaceous matrix is identical to tuffs characteristic of the upper Bully Hill rhyolite and lower Pit formation elsewhere in the Bully Hill area. Bedding attitudes within the blocks of sediments may be subconformable to the local lithological layering or possess chaotic orientations. These characteristics led to the interpretation by Eastoe et al. (1987) that the lower Pit formation is an olistostromal megabrecchia.
Unaltered andesite of the upper mafic unit of the Bully Hill rhyolite is exposed west of the northernmost extent of the Type 1 alteration zone on the west limb of the anticline. The limits of the andesite were not mapped, but it is probably part of a large andesitic body mapped by Albers and Robertson (Plate 1, 1961). An additional occurrence of unaltered andesite is found in a single outcrop within the volcaniclastic deposit west of the trench at the Copper City mine. This is either an exposure of a small intrusion or a block within the slump deposits.

Shasta May Blossom Prospect

The Shasta May Blossom prospect is located approximately 2.5 kilometers east of Bully Hill (Figure 2). There is no recorded production from the prospect, although a few sulfide lenses and some precious metal-rich mineralization is reported to have been intersected by the fairly extensive underground workings (Tucker, 1923).

The Shasta May Blossom prospect was examined briefly. A sketch map of the geology is presented in Figure 13. As is the case in the Bully Hill-Rising Star and Copper City mine areas, the Shasta May Blossom is located on a hill which is somewhat higher than its immediate surroundings, owing to the presence of intensely silicified rocks.

A curvilinear zone of intensely silicified breccia consisting of angular fragments of volcanic(?) rocks and
Figure 13. Sketch geologic map of the Shasta May Blossom prospect. Symbols are the same as in Figures 4 and 12. Map base: 15' topographic map
fine-grained sediments of the Pit formation forms the ridge-line of the hill. The intensity of silicification in this zone is similar to that in the Type 1 alteration zones previously described, but it is much less extensively developed and no stockwork mineralization is present. Gossanous layers up to a few tens of centimeters thick are locally interlayered with intensely silicified fine-grained sediments within this zone. Albers and Robertson (1961) reported that the gossan layers are up to six meters thick.

Aphanitic andesitic lava outcrops stratigraphically below the silicified zone. The lava consists of abundant plagioclase microlites, locally forming radial aggregates, in a glassy to microspherulitic intersertal groundmass. Up to 5 volume percent pyrite is disseminated in the groundmass. The andesite is part of the upper mafic unit of the Bully Hill rhyolite.

Fine-grained sediments and interbedded orange-weathering lithic coarse lapilli tuff of the Pit formation overlie the silicified zone. Lithic fragments in the tuff are subrounded, up to at least ten centimeters in the longest dimension, and consist of quartz ± plagioclase-phyric rhyodacitic volcanic rocks. Lithic fragments containing up to 50% sulfide are found locally in the tuff. A large, apparently disconformable mass of this tuffaceous material occurs on the eastern limits of the map area. On the easternmost edge of this body, at what may be the stratigraphic
top, are large blocks of silicified and mineralized mudstones and siltstones of the Pit formation, unaltered quartz and feldspar-phyric rhyodacitic volcanic rocks and unaltered Pit sediments.

The general chaotic lithologic pattern in the area of the Shasta May Blossom prospect and the presence of the orange-weathering lithic tuff with exotic blocks suggests that the andesitic volcanic mass capped by the silicified breccia may be one large block within the olistostromal megabreccia of the lowermost Pit formation.

Reconnaissance Geology of the Bully Hill Rhyolite and Lowermost Pit Formation

Using the geologic map of Albers and Robertson (1961) as a base, several transects through the Bully Hill rhyolite in the Bully Hill area were investigated. This section reviews significant geologic features of the Bully Hill area not covered in the preceding sections.

Albers and Robertson (1961) identified a vent for the silicic volcanic rocks of the Bully Hill rhyolite about 1 kilometer northeast of Bully Hill. Evidence cited for the existence of the vent includes the abundance of pyroclastic material, the unusual thickness of the Bully Hill rhyolite, the heterogeneous lithologies and the presence of a circular mass of porphyritic lava with inward-dipping flow-banding -- suggestive of a cumulo dome -- in this area (Figure 2).
Additional evidence from this study includes a felsic dike within the cumulo dome, the only dike recognized within the Bully Hill rhyolite in the entire Bully Hill area, and the presence of exotic blocks of felsic plutonic rock immediately west of the vent within agglomerate of the lower tuff unit at Bully Hill. These large fragments were presumably transported from a basement source as xenoliths in the source magma and extruded from a nearby vent.

An additional vent in the area of the Copper City mine may have extruded the dacitic lavas that form the base of much of the Bully Hill rhyolite in the western portion of the Bully Hill area.

To the north and east of the cumulo dome, the outcropping width of the Bully Hill rhyolite expands significantly owing to the combination of shallow dips and topographic effects. The uppermost tuffaceous unit in this area is the quartz-phyric orange tuff characteristic of the upper Bully Hill rhyolite and lower Pit formation. Four bodies of the upper mafic unit of the Bully Hill rhyolite, including the andesite at the Shasta May Blossom prospect, are included within this mass of orange tuff (Figure 2).

Another body of mafic rock occurs one kilometer southwest of Copper City. This portion of the upper mafic unit is composed predominantly of unaltered mafic volcanogenic sediments and tuffaceous rocks with subordinate lavas. Minor greywacke, hematitic chert and a dense, aphanitic,
flow-banded basaltic lava with columnar jointing are also present within this exposure.

Orange tuff underlies this mafic body on at least its southwesternmost exposure, is locally interlayered with the mafic rocks, and overlies the body. Attitudes in the upper portion of the mafic body are often discordant to those of the overlying orange tuff, which is part of the chaotic orange tuff-Pit sediment megabreccia typical of the lower Pit formation in this area.

The southwesternmost exposure of Bully Hill rhyolite consists of flow-banded plagioclase ± hornblende-phyric dacite with an autobrecciated and moderately silicified top. The lava is overlain by the orange tuff-Pit sediment megabreccia, which in this area contains fragments of flow-banded dacite. The lava is underlain by various dacitic volcanic rocks which Albers and Robertson (1961) placed within the Dekkas formation. A zone of intensely silicified and pyritized breccia is exposed within the dacitic rocks a short distance below their contact with the lava.

The placement of the contact between the Bully Hill rhyolite and Pit formation at the first appearance of mudstone (Albers and Robertson, 1961) may not have paleoenvironmental significance due to the identical lithology of the orange tuff in the upper Bully Hill rhyolite and lower Pit formation and the interpretation that the lower Pit formation is an olistostrome. Reconnaissance field evidence
suggests that much of the uppermost Bully Hill rhyolite is part of the same lithologic package as the lower Pit formation. The six bodies of the upper mafic unit in the Bully Hill area (Figure 2) are all closely associated with, and perhaps completely enclosed within, the orange tuff of the upper Bully Hill rhyolite and lower Pit formation. These mafic bodies may all be blocks within the megabreccia.
CHAPTER 4

STRUCTURE OF THE BULLY HILL AREA

Primary Foliations

Bedding attitudes were measured on sediments of the Pit formation and tuff beds within the Bully Hill rhyolite. Although overturning of some beds in the eastern portion of the Bully Hill-Rising Star map area is suspected (Figure 5), no definite field evidence of this was seen and the attitudes are presented as upright on Figure 4. The limited bedding data at Bully Hill are consistent with a north-south-trending fold with a south-plunging axis (Figure 14).

Flow-banding is common in the lava unit of the Bully Hill rhyolite. This flow foliation is commonly contorted and folded unsystematically, forming primary deformational structures. Where the strike of the flow foliation is consistent, such as adjacent to lithologic contacts where the strike is often subparallel to the contact, attitudes were recorded. Even in these areas, however, dips of the flow-banding are usually quite variable.

Folds

A tight south-plunging anticline, which is overturned to the east in the northern half of Figure 4,
Figure 14. Equal area stereonet projection of poles to bedding. 20 data points.

Figure 15. Spaced cleavage developed in outcrop of silicified lava.
forms the dominant structural feature of the Bully Hill-Rising Star mine area (Figures 4 and 5). The axial trace of the fold trends generally north to north-northeast, with topographic considerations indicating that the axial surface is steeply dipping to the west. Although the presence of the anticline is indicated by the pattern of lithologic contacts within the Bully Hill rhyolite, the geometry of the fold is defined primarily by the map pattern of the Type 1 alteration zones (Figure 6).

Data compiled by Albers and Robertson (1961) from underground workings of the Bully Hill and Rising Star mines provide evidence of the morphology of the anticline. Two cross-sections showing the contact of their porphyritic quartz keratophyre (lava unit) and metadacite tuff (upper tuff unit) in the area of the Bully Hill mine workings indicate that this contact is overturned near the surface (Plate 11, Albers and Robertson, 1961). At the Rising Star mine, consideration of the cross-sectional outlines and three-dimensional geometry of the lenses of massive sulfide suggests that the anticline is not overturned in this area and that the axial surface of the anticline may dip steeply to the west, if one assumes that the lenses are grossly conformable to primary layering (Plate 10, Albers and Robertson, 1961; Figure 11). Massive sulfide lenses on the east limb of the fold are elongate, suggestive of cross-sections of steeply-dipping lenses similar to those seen in the Bully
Hill mine, and mine-level-to-mine-level projections of the lenses suggest that they dip steeply to the east. Projections of massive sulfide lenses on the west limb of the fold suggest that they dip to the west. Cross-sections of these lenses are somewhat oblate, suggestive of more moderate dips than those of the east limb.

Albers and Robertson (1961) identified a tight southeast-plunging syncline in the Pit formation east of the Bully Hill-Rising Star map area. Immediately east of the Bully Hill mine area this fold is also overturned to the east.

The north-trending anticline in the Copper City area is probably related to these folds at Bully Hill. Sparse bedding attitudes and the general geomorphic expression of the ribs of Type 1 alteration suggest that the axial surface of the fold may dip steeply to the west. The trace of the axial surface bends sharply to the northwest north of the Copper City map area (Albers and Robertson, 1961).

These tight north to northeast-trending folds at Bully Hill and the Copper City mine area, and several other folds with similar trends in the Bully Hill area identified by Albers and Robertson (1961), are in contrast to the predominant pattern of more open northwest-trending folds throughout the East Shasta district.
Spaced cleavage

A distinctive spaced cleavage is characteristically developed within the anticlinal structure at Bully Hill in mechanically isotropic rocks. The cleavage is most prevalent in massive, highly silicified flows of the lava unit within Type 2 alteration zones. It is weakly developed or absent in less silicified areas and in inhomogeneous lithologies, such as autobrecciated lavas and lithic tuff breccias.

The spaced cleavage is characterized by well-defined regularly-spaced cleavage domains typically 2 to 15 centimeters apart separated by unfoliated lithon domains. The cleavage domains form anastomosing patterns at both thin section and outcrop scales, resulting in lozenge-shaped lithon domains (Figure 15).

Cleavage domains consist largely of sericite; hematite is also common in weathered exposures. In thin section, anastomosing cleavage domains truncate quartz phenocrysts, a texture clearly formed by dissolution of the quartz.

Spaced cleavage generally strikes north-south and has subvertical dips (Figure 16). It is interpreted that the cleavage is an axial planar foliation of the anticline.

Chemical changes accompanying spaced cleavage formation are discussed in CHAPTER 7.
Figure 16. Equal area stereonet projection of spaced cleavage. a. poles to cleavage b. 1, 5 and 10% contours per 1% area. 63 data points

Figure 17. Equal area stereonet projection of schistosity. a. poles to schistosity b. 1, 5, 10 and 15% contours per 1% area. 37 data points
Schistosity

In the Bully Hill-Rising Star mine area, schistosity is observable within the matrix of many of the lithic tuffs and in any lithology which contains a significant percentage of sericite. Schistosity dips to the east and west at high angles and strikes northwest (Figure 17). This orientation parallels the principal structural grain of the East Shasta district (Albers and Robertson, 1961), and is interpreted to be an axial planar foliation of this regional northwest-trending fold set.

No cross-cutting relationships between the spaced cleavage and schistosity were noted. It is interpreted that the broad district-wide northwest-trending folds are younger than the apparently localized, tight north-trending folds at Bully Hill, since the schistosity is not reoriented by the event which formed the spaced cleavage. The spaced cleavage also shows no evidence of being reoriented, but this is not surprising since: (1) northwest-trending folds are not recognized in the area in which the spaced cleavage occurs; and (2) the spaced cleavage is developed as a phenomenon of pressure solution in massive silica-rich rocks which otherwise would exhibit no deformational foliation, and since the lithon domains enclose the volumetrically less abundant cleavage domains, no overprinting of the cleavage orientations by a younger schistosity is expected. Albers and Robertson (1961) also concluded that north-trending folds
predated the northwest fold set on the basis of district-wide relationships.

The tight, partially overturned folding in the immediate vicinity of Bully Hill is interpreted to have formed as a consequence of the rheological contrast between intensely silicified rocks of the Bully Hill rhyolite and the clay-rich lithologies of the upper Bully Hill and lower Pit formations. This inherent competency contrast could have allowed rocks in this area to accommodate anomalous amounts of strain during the earlier deformation. Additional detailed mapping in the Bully Hill area would most likely reveal further manifestations of this early deformation.

Faults

Several faults are recognized in the Bully Hill-Rising Star map area, the most significant of which have northwesterly strikes. Two of these structures have obvious economic significance. The first is a long shear zone which is best exposed in the northwest-trending gully north of the Rising Star mine (the East shear zone of Albers and Robertson (1961)). This shear zone truncates the Type 1 alteration zone of the Rising Star area on both limbs of the anticline. In the underground workings, the shear zone apparently truncates the massive sulfide horizons of the Rising Star mine on the east limb of the fold; no further mineralization was mined to the north of the structure.
(compare Figures 4 and 11). North of the shear zone on the surface, the continuation of Type 1 alteration of the east limb is offset approximately 60 meters to the east. This possible continuation of the Rising Star mine mineralization has not been prospected.

The other fault of possible economic significance at Bully Hill truncates the Type 1 alteration zone northwest of the Rising Star shaft on the west limb of the anticline. This fault also appears to truncate ore horizons, on the basis of underground stoping data (compare Figures 4 and 11). The continuation of the Type 1 alteration zone and possible associated mineralization across the structure to the northwest has apparently not been prospected in detail.

Albers and Robertson (1961) reported that the contact between the lava and upper tuff units is a shear zone in the area of the Bully Hill mine, largely on the basis of underground exposures. Noting that bedding in units adjacent to the structure is conformable to the sheared contact, they stated that the shear zone "probably ... formed as a result of shearing and bedding slippage along the contact between units of greatly different competencies" during the folding event which produced the north-northeast-trending folds, and that "net displacement was probably small".
In the Copper City mine area, several faults of minor displacement are identified by offsets in the Type 1 alteration zones.
CHAPTER 5

MINERALIZATION

Introduction

Descriptions of the styles of mineralization in the Bully Hill area are included in this chapter; detailed petrographic descriptions of various massive sulfide-sulfate ore types are presented in CHAPTER 8.

Bully Hill-Rising Star Mines

Three principal styles of mineralization are present in the Bully Hill-Rising Star mine area: vein stockwork zones, massive sulfide ores with or without banding and bedded fine-grained barite. The stockwork mineralization is essentially restricted to Type 1 alteration zones, and was described in CHAPTER 3.

The massive sulfides occur as clusters of small lenticular bodies (Figure 11). Individual lenses range up to 100 meters in length and 10 meters in width (Albers and Robertson, 1961). They are composed primarily of various combinations of pyrite, sphalerite, galena, chalcopyrite and tetrahedrite-tennantite in a fine-grained baritic matrix. Pyrite, chalcopyrite and sphalerite-rich ores are three
common endmembers which occur as individual lenses and as bands within lenses (Albers and Robertson, 1961).

An additional endmember of the massive ores is represented by fine-grained barite ± sulfide (Figure 18). The massive barite occurs as discrete lenses and as bands within massive sulfide bodies. Individual lenses of massive, bedded barite occur in the Bully Hill mine area and are closely associated with the massive sulfide lenses.

Lenses of gypsum and anhydrite up to 25 meters long and 10 meters thick are reported from the Bully Hill mine workings (Albers and Robertson, 1961). Masses of gypsum and anhydrite also partially engulf massive sulfide lenses in the lower levels of the Bully Hill and Rising Star mines.

The lenses of massive sulfide, barite and gypsum-anhydrite in the Bully Hill mine lie along several horizons which occur at or immediately adjacent to the contact between the lava unit and the upper tuff unit (Plate 11, Albers and Robertson, 1961; Figure 11). The horizons are conformable with this contact. At the Rising Star mine the massive sulfide lenses occur in at least two closely-spaced horizons within the lower portion of the lava unit (Figure 11). These horizons outline the nose of the anticline which dominates the structure at Bully Hill, and therefore are at least grossly conformable to primary layering in this area.
Figure 18. Fine-grained banded massive barite. Sample BHO.

Figure 19. Block of massive barite within orange tuff of lower Pit formation.
Copper City Mine

Stockwork and massive sulfide-barite mineralization similar to that of the Bully Hill-Rising Star mine area is also present at the Copper City mine. Calcitized tuff with minor pyrite and sphalerite also occurs in several dumps of small prospects along the Copper City horizon.

Shasta May Blossom Prospect

The numerous prospects on the hill of the Shasta May Blossom area explore the silicified zone. Styles of mineralization found in dumps of these prospects include silicified quartz-phyric lithic tuffs with pods and disseminations of carbonate and pyrite, and andesite partially replaced by sulfides, calcite and barite. In the andesite, the first stage of mineralization is represented by disseminated pyrite in the groundmass. This was followed by coarse blades of barite with or without minor quartz which replaced glass and pervaded the rock along irregular veinlets. Calcite then partially replaced the barite and further pervaded the groundmass. This was followed by idiomorphic pyrite, trace sphalerite and chalcopyrite, quartz, sericite and minor barite. This stage formed semi-massive sulfide replacement pods within the andesite. A late calcite stage replaced plagioclase microlites and glass, and terminated the alteration sequence.
Other Mineralization

Finely-banded massive sulfide ore occurs in a small dump from a covered prospect approximately one kilometer west-southwest from Copper City (Sample site SH-45, Figure 2). Although there is very little exposure in the area, this occurrence is correlated with the projection of the Copper City horizon. About 100 meters of silicified and pyritized volcanic rocks are exposed in a creek 200 meters northeast of the prospect.

A thin bed of carbonate-rich tuff is exposed in Horse Creek at the GE-59 sample site (Figure 2). The carbonate bed is approximately 20 to 30 centimeters thick, and is intercalated with thinly-bedded quartz + plagioclase crystal tuffs and tuffaceous mudstones of the Pit formation. These volcanogenic sediments overlie an agglomerate of the uppermost Bully Hill rhyolite. The carbonate-rich tuff consists of 80 volume percent coarsely crystalline calcite. The calcite replaces the quartz-rich ash matrix, quartz and plagioclase crystal fragments, and thin layers and disseminations of pyrite and trace sphalerite. Similar calcitized tuffs are found in dumps from prospects in the Copper City area.

A 40 m x 40 m x 10 m block of massive barite occurs within the Pit formation along the shoreline of Shasta Lake 1 kilometer southwest of Copper City (Sample site SH-40; Figure 19). Lake level must be low for the block and sur-
rounding orange tuff to be fully exposed. The block consists of a central area of a coarsely crystalline barite ± pyrite stockwork of veins which cut a matrix of coarsely-crystalline massive barite. The periphery of the block is composed of a coarse breccia made up of fragments of the main mass of the block cut by additional barite veins. The barite block probably formed as a mound from Ba-rich solutions exhaled onto the seafloor. The block appears to be a fragment within the olistostromal megabreccia.

Another block within the megabreccia occurs approximately 0.5 kilometers north of the barite block at sample site SH-41 (Figure 2). This block consists of Type 1 altered Pit mudstone with the accompanying quartz and barite veinlet stockwork. Barite fills voids in and partially replaces the quartz.
CHAPTER 6

GEOLOGICAL SYNTHESIS OF THE BULLY HILL AREA

Mineralization Genesis

The mineralization of the Bully Hill area is clearly volcanogenic, i.e., consanguineous with the volcanic rocks. Evidence of this includes:

(1) asymmetry of hydrothermal alteration. Intense silicification ± sericitization ± pyritization is characteristic of rocks stratigraphically below the Bully Hill and Copper City ore horizons. Rocks stratigraphically above these horizons show little to no effect of hydrothermal circulation.

(2) transported fragments of hydrothermally altered and mineralized rocks occur in subsequent deposits within the volcanic pile. Fragments of volcanic rocks silicified prior to incorporation into subsequent fragmental deposits are common in reworked lithic tuffs in the Bully Hill-Rising Star, Copper City and Shasta May Blossom areas. The blocks of massive barite and Type 1 altered Pit sediments within the olistostrome deposit of the lower Pit formation are large-scale examples. At the Rising Star mine a boulder of conglomerate containing rounded sphalerite-rich massive sulfide clasts was found in a dump. The fragmental massive
sulfide ore and the volcaniclastic rock with barite clasts exposed in the area of the trench at the Copper City mine are further examples of reworked mineralization.

The designation of syngenetic or epigenetic to the various styles of mineralization is made difficult because of the inaccessibility of the underground workings. The stockwork mineralization of the Type 1 alteration zones is clearly epigenetic. Although replacement textures between sulfide minerals in the massive ore are common (see CHAPTER 5) it is probable that much of this mineralization is syngenetic. Evidence of this is the stratiform and stratabound nature of both the massive ore horizons and sulfide lenses.

Albers and Robertson (1961) believed that the massive sulfide mineralization in the East Shasta district was entirely epigenetic, formed by replacement of the host rocks long after their deposition. At the Bully Hill mine, they believed that the conformable shear zone which separates the lava and upper tuff units localized the ore-bearing solutions. In the case of the Rising Star mine, they believed the ore bodies were genetically related to several shear zones which are clearly discordant to lithologic contacts as defined in this study. They conceded, however, that "the relation between the larger sulfide lenses and shear zones [in the Rising Star mine] is obscure".

Evidence cited by Albers and Robertson (1961) for their interpretation that the massive ores are epigenetic
replacement bodies included: blocks of country rock within sulfide lenses in which layering in the horses and banding of the sulfides is conformable; banding in the sulfides which parallels bedding in adjacent rocks; and the gradational change in sulfide content from the massive ores to barren country rock. The lack of crustification textures was cited by the authors to support a replacement versus fissure-filling origin for the ores. All of this evidence could also be used to argue for a syngentic origin of the massive sulfide ores, an option which had not been widely recognized at the time of the study of Albers and Robertson.

**Correlation of Mineralized Horizons/Economic Favorability**

Figure 2 shows the interpreted extensions of the Rising Star, Copper City and Bully Hill horizons throughout the Bully Hill area. The regional placement of these horizons is based on reconnaissance geologic work and a reinterpretation of the geologic map of Albers and Robertson (1961). The mineralization of the Copper City and Bully Hill mines is shown as being coeval, and younger than the Rising Star horizon, since both may lie immediately below the olistostrome of the upper Bully Hill rhyolite and lower Pit formation. The Shasta May Blossom mineralization may have been transported to its present position, and is therefore not projected beyond the prospect area on Figure 2.
The Bully Hill-Rising Star mine area has obvious potential for additional massive sulfide mineralization. The long north-trending exposures of Type 1 alteration north of the Rising Star mine area are interpreted to be the faulted extensions of the folded Rising Star Type 1 zones. These extensions are virtually unprospected on both limbs of the anticline. Silicification and sulfide-barite mineralization is particularly intense near the summit of Bully Hill, which is stratigraphically directly below the productive portion of the Bully Hill mine horizon. Unrecognized faults and/or fracture zones which may have localized mineralizing fluids at the Bully Hill mine could have been reactivated structures which initially funneled ore-forming solutions to the Rising Star horizon. The Rising Star horizon quickly loses definition in the Bully Hill area, and further potential of this horizon beyond this area is probably limited.

The southern extension of the Bully Hill mine horizons is also highly prospective. In the area of the nose of the Rising Star mine, the lava and tuff breccia units are highly silicified between their contact with the upper tuff unit and the Rising Star Type 1 alteration zone (Figure 6). Pyritization of the lavas and tuff breccia near the hanging-wall contact is locally intense. Barite veins, many of which appear to have been remobilized during deformation of this area, are also common. The possibility of reactivating
hypothetical feeder structures of the Rising Star mineralization enhances the economic potential of this area.

The northern extension of the Bully Hill mine horizon beyond the area of Figure 4 is folded around the nose of the syncline identified by Albers and Robertson (1961) (Figure 2). In this area the horizon is the contact between intensely silicified and pyritized flow-banded quartz-phyric rhyodacitic to rhyolitic lava and the overlying orange tuff. The alteration appears to be spatially restricted to the immediate footwall of the contact, but since the ore lenses in the Bully Hill mine plunge approximately 70° north as a group, further mineralization to the north may be deep and surface manifestations of the hydrothermal system may be subtle. Further exploration in this area is warranted.

At Copper City, the entire length of the horizon stratigraphically overlying the Type 1 alteration zone has not been extensively prospected. Although the mineralization associated with the Type 1 alteration is not as well-developed as in the area of Bully Hill, the Copper City area has definite potential for further massive sulfide mineralization.

Southwest from Copper City, the Bully Hill-Copper City horizon is interpreted to pass through the prospected massive sulfide mineralization approximately 1 kilometer west of Copper City (sample site SH-45), below the body of mafic volcanic rocks and through the contact of the Pit
formation and the moderately silicified autobrecciated dacitic lavas in the southwesternmost part of the Bully Hill area. Albers and Robertson (1961) mapped a fault along a segment of the horizon in this area. The portion of this horizon between Copper City and the massive sulfide occurrence to the west appears to have the highest potential for further undiscovered mineralization. The potential of the Bully Hill-Copper City horizon between Copper City and Bully Hill and in the northeastern portion of the Bully Hill area beyond the cumulo dome is unknown but probably low.

The Shasta May Blossom area is not considered highly favorable for prospecting owing to the lack of intense alteration, the restricted areal extent of the alteration and the absence of significant sulfide or sulfate mineralization.

Geologic History of the Bully Hill Rhyolite

The following discussion integrates the field data from this study with the district-wide data set of Albers and Robertson (1961). Reference to Figure 20, which presents a reconstructed cross-section through the Bully Hill rhyolite, and Figure 2 is helpful.

Initial eruptions from a subaqueous vent northeast of Bully Hill consisted of feldspar-phyric dacitic lavas which are presently exposed in the lowermost Bully Hill rhyolite west of the cumulo dome. Pyroclastic eruptions and
Figure 20. Generalized reconstructed cross-section of the Bully Hill rhyolite in the Bully Hill area. Black lenses are massive sulfide accumulations of the Bully Hill (bh), Rising Star (rs) and Copper City (cc) mines. Rocks of the upper mafic unit are not represented.
extrusions of quartz + feldspar-phyric lavas followed, along with slumping of the growing felsic pile near the vent. The resulting talus-breccias formed the lower tuff unit at Bully Hill.

Feldspar ± hornblende-phyric lavas may also have vented in the Copper City area. These dacitic lavas covered an area from Horse Creek to the westernmost extent of the Bully Hill rhyolite in the Bully Hill area. This magmatic center was small, and did not evolve to include more felsic extrusions.

Quartz and feldspar-phyric rhyodacitic to rhyolitic lava extrusion began building the cumulo dome, and lava flowing down the cumulo dome formed the autobrecciated lavas of the lower portion of the lava unit at Bully Hill. A pause in volcanic activity allowed a hydrothermal system which had been developing to vent metal-rich fluids onto the seafloor along the Rising Star horizon for a period of time sufficient to form the massive sulfide bodies.

This hydrothermal episode was followed by voluminous extrusions of porphyritic rhyodacitic to rhyolitic lava and subordinate pyroclastic material which formed the bulk of the cumulo dome and the lava unit. The extrusions of lava flowed in a westerly direction, off the topographic high of the cumulo dome and into a basin at Bully Hill. Pyroclastic eruptions and slumping of debris off the dome succeeded the extrusions of lava, and formed the tuff breccia unit. As
volcanic activity waned, hydrothermal systems were again able to exhale metal-rich solutions onto the seafloor for an extended period, and the mineral deposits of the Bully Hill and Copper City horizons were formed. Pelagic sedimentation in areas distal from the vent (Copper City area) began to dominate.

Felsic pyroclastic eruptions and slumping of material off the dome buried the massive sulfide deposits at Bully Hill, forming the upper tuff unit. Extensional stresses formed structures which tapped deeper mafic magma, mafic sills were intruded into the uppermost portion of the felsic pile at Bully Hill, and andesitic to basaltic volcanic rocks were extruded throughout the Bully Hill area. Limited hydrothermal activity following deposition of the mafic volcanics formed the Shasta May Blossom mineralization. Continued extension caused the formation and subsequent seismically-induced collapse of unstable fault scarps of felsic pyroclastic material, pelagic sediments and minor mafic volcanic material. The resulting olistostrome(s) excavated the mineralization of the Shasta May Blossom prospect and a portion of the mineralized rocks in the Copper City area, and buried the entire Bully Hill area, forming the uppermost Bully Hill rhyolite and lower Pit formation.
CHAPTER 7

WHOLE ROCK GEOCHEMISTRY

Introduction

In order to classify rock types and study geochemical changes accompanying the hydrothermal alteration in the Bully Hill area, thirty-nine rock samples were analyzed for their major element and barium contents. Zirconium, titanium, yttrium, and niobium were also determined for twenty-two of these samples (Table 2). The samples are located in Figures 2 and 21.

Lithological Classification

Classification on the Basis of Major Element Chemistry

Hughes Plot. Albers and Robertson (1961) categorized the rocks of the Dekkas andesite and Bully Hill rhyolite as spilites, keratophyres, and quartz keratophyres on the basis of major element compositions and petrographic observations. In order to evaluate these designations, analyses of various volcanic rocks of the Bully Hill area are presented on a diagram proposed by Hughes (1972) to differentiate unaltered igneous Na₂O and K₂O contents from those characteristic of spilites, keratophyres, and quartz keratophyres (Figure 22). The samples plot in four areas on
Table 2. Chemical compositions of selected samples from the Pit formation, Bully Hill rhyolite and Dekkas andesite. FeO\textsubscript{t} is total iron. * denotes analyses by TML; all other analyses by XRAL; DK = Dekkas andesite; Um = upper mafic unit; LV = lava unit; Tf = lithic-rich tuff; Qp = quartz-phyric lava; Np = quartz phenocryst-poor felsic lava

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Figure 21. Simplified geologic map of the Bully Hill-Rising Star mine area, showing sample locations. Symbols are the same as in Figure 4.
Figure 22. Alkali differentiation diagram of Hughes (1972). Dashed line encloses field of highly altered samples from the Bully Hill-Rising Star mine area.
the Hughes diagram: within the igneous spectrum; in the field of spilites, keratophyres, and quartz keratophyres to the left of the igneous spectrum; in an unusual position to the right of the igneous spectrum; and below the igneous spectrum. Although the diagram serves to grossly differentiate the degree of hydrothermal alteration in these samples, it is an inadequate discriminator of original lithologies.

Samples plotting within the igneous spectrum and the spilite/keratophyre fields represent the bulk of the Dekkas andesite and Bully Hill rhyolite. Within the igneous spectrum, the diagram classifies samples of the lava unit, other quartz-phyric lavas and the feldspar-phyric lavas as dacites. The samples of the lava unit plot anomalously sodic. The sample from the upper mafic unit of the Bully Hill rhyolite that lies within the igneous spectrum plots as a tholeiite, and the sample of Dekkas andesite plots as an alkali basalt. Samples lying within the spilite/keratophyre field are characterized by anomalously low K/K+Na ratios due to the metastasomatic replacement of K⁺ by Na⁺ in feldspars (the process of keratophyrization or albitization).

All samples from within the area of visible hydrothermal alteration in the Bully Hill-Rising Star mine area (alteration Types 1-6) plot to the right of the igneous spectrum. These samples form a crude trend from least to most altered, which indicates that total alkali contents, as
expressed in weight percentages, decrease while $K/K+Na$ ratios increase with increasing degree of hydrothermal alteration. Decreasing alkali contents are probably caused by a combination of hydrothermal leaching of the alkalis and dilution by addition of other components, especially $SiO_2$. The increased $K/K+Na$ ratios are reflected by the presence of secondary sericite in the highly altered rocks.

Two samples lie in a unique position below the igneous spectrum in Figure 22. These samples are relatively unaltered, lying stratigraphically above the Bully Hill-Copper City horizon remote from the massive sulfide mineralization. They are characterized by low total alkali concentrations.

The Hughes diagram identifies two distinct varieties of alteration in the Bully Hill area: keratophyrization and the hydrothermal alteration associated with massive sulfide formation. The alteration of the intermediate to felsic volcanic rocks to keratophyres and quartz keratophyres is a manifestation of a regional low-temperature interaction between the volcanic pile and relatively cool seawater. This alteration was locally overprinted by a high-temperature hydrothermal system(s) which produced the massive sulfide mineralization.

Jensen Cation Plot. Jensen (1976) presented a ternary plot used to classify subalkalic volcanic rocks. The classification is independent of components which are highly
mobile in hydrothermal systems, such as Na$_2$O, K$_2$O, CaO, and SiO$_2$. FeO, Fe$_2$O$_3$, TiO$_2$, MgO, and Al$_2$O$_3$, relatively stable components, are utilized instead.

The Dekkas andesite samples span the calc-alkaline field compositions from dacite to basalt. The felsic rocks from the Bully Hill area lie predominantly within the calc-alkaline field of the Jensen cation plot (Figure 23). Miller (1989), on the basis of trace element data, and Lapierre et al. (1986) and Martin et al. (1984), on the basis of major element data, characterized the volcanic rocks of the Nosoni formation and Dekkas andesite as island arc tholeiites.

Lava unit samples plot primarily in the rhyolite field, and other quartz-phyric lavas and feldspar-phyric lavas lie primarily within the dacite field. Pyroclastic rocks plot throughout the compositional range in the calc-alkaline field.

Both samples of the upper mafic unit lie within the andesite field, one plotting on the tholeiitic side and the other on the calc-alkaline side.

The scatter of samples from the lava unit on the Jensen cation plot suggests that although the Jensen diagram crudely classifies the samples, the ore-related hydrothermal alteration affected at least some of components used in the diagram. Classification of original lithologies in the
Figure 23. Jensen Cation plot (Jensen, 1976) of volcanic rocks from the Bully Hill area. Symbols are the same as Figure 22.
Bully Hill area based on major element compositions is therefore inadequate.

Classification Based on Trace Elements

**Winchester and Floyd Diagram.** Winchester and Floyd (1977) presented a discrimination diagram for igneous rocks based on trace elements which have been shown to be immobile during such processes as metamorphism, keratophyrization, submarine alteration and, in some cases, extreme hydrothermal alteration. The plot utilizes ratios of the immobile elements, so that alteration processes involving net changes in mass will not affect the classification.

Samples of the lava unit form a tight group which straddles the rhyodacite-rhyolite boundary of the Winchester and Floyd diagram (Figure 24). The single deviant from this group is a sample from the Type 1 alteration zone immediately below the Bully Hill horizon (BH-27), which lies in the rhyolite field to the right of the group. The single sample of other quartz-phyric lavas lies within the dacite/rhyodacite field. The feldspar-phyric lavas form a group in the lower portion of the dacite/rhyodacite field.

One sample of the upper mafic unit lies within the andesite field and the other in the lowermost portion of the andesite/basalt field. This distinction is consistent with field and petrographic observations. The pyroclastic samples are scattered throughout the dacite/rhyodacite
**Figure 24.** Plot of Zr/TiO$_2$ versus Nb/Y (Winchester and Floyd, 1977) for volcanic rocks in the Bully Hill area. Symbols are the same as in Figure 22.
field. The samples of Dekkas andesite lie within the andesite and basalt fields, and as a group appear to have compositions which are distinct from upper mafic unit lithologies.

The positioning of BH-27 to the right of the cluster of lava unit samples suggests that Nb and/or Y were mobile during Type 1 alteration. The overall coherence of the Winchester and Floyd classification, however, suggests that Zr and Ti were largely immobile in all samples, and validates the use of the Winchester and Floyd diagram as a lithologic discriminator for the Bully Hill volcanic rocks.

Conclusions

The Winchester and Floyd diagram allows classification of the original lithologies in the Bully Hill area. Volcanic rocks of the Dekkas andesite are primarily andesitic in composition, with subordinate basalts. This composition is in contrast to the dominance of basaltic volcanic rocks in the Dekkas andesite north of the Bully Hill area (Miller, 1989) and in the Afterthought mine area (Eastoe and Nelson, 1988). The lower, feldspar-phyric portion of the Bully Hill rhyolite is dacitic in composition. The overlying quartz-phyric lavas consist of rhyodacite to rhyolite. The lithic-rich pyroclastic rocks of the Bully Hill rhyolite and Pit formation appear to have a bulk composition in the dacitic to rhyodacitic range.
The upper mafic unit contains both andesite and basalt. Two samples of the upper mafic unit in the Afterthought mine area plot as sub-alkaline basalt on the Winchester and Floyd diagram (Eastoe and Nelson, 1988).

The Bully Hill area data suggest that the volcanic rocks of the Dekkas andesite and Bully Hill rhyolite represent a magmatic differentiation trend from basalt and andesite (Dekkas andesite) to dacite (lower Bully Hill rhyolite) to rhyolite (lava unit of upper portion of the Bully Hill rhyolite). Lapierre et al. (1986) came to a similar conclusion. The presence of basaltic volcanics of the upper unit indicates that the volcanism became bimodal, and is suggestive of rifting during deposition of the Bully Hill rhyolite (Eastoe and Nelson, 1988).

It is evident from the Hughes diagram that the bulk of the Bully Hill rhyolite has been altered to quartz keratophyre. The failure of the Hughes plot to adequately classify the least-altered samples confirms that even these samples have been altered to some degree.

**Chemical Changes Accompanying Hydrothermal Alteration**

**Introduction**

The lava unit of the Bully Hill rhyolite is the most extensive and lithologically consistent map unit in the Bully Hill area. The unit extends from the lava dome northeast of Bully Hill, through the most intense alteration
zones of the Bully Hill-Rising Star mine area, and then beyond the area of alteration to Horse Creek (Figure 2). These characteristics make the lava unit ideal for a study of the chemical differences of least-to most-altered rocks.

Figure 25 shows the positioning of the samples of the lava unit relative to a generalized reconstructed cross-section of the Bully Hill area. BH-27, BH-28 and BH-29 are from Type 1 alteration zones, BH-14 and BH-63b are from Type 2 alteration zones, BH-234 is a sample of Type 3 alteration near the hypothesized extension of the Rising Star horizon, and BH-58 is representative of relatively unaltered quartz keratophyre (see Figure 22). BH-3, BH-145 and BH-232 are samples of relatively unaltered lavas from Type 7 alteration zones distal from the orebodies.

Methodology

Comparison of weight percent oxide values in an evaluation of gains and losses of chemical components during hydrothermal alteration processes is valid only in cases of metasomatic replacement involving no net change in mass from unaltered protolith to altered product. In an alteration reaction involving a net mass change, a density and/or volume change must also occur. Calculations of losses and gains of chemical components based on the assumption of constant volume or density may therefore lead to serious errors. Gresens (1967) presented a mass balance calculation
Figure 25. Idealized reconstructed cross-section of the Bully Hill-Rising Star mine area showing distribution of alteration Types 1 through 5, syngenetic ore lenses (solid black bodies) and lava unit sample locations. Symbols are the same as in Figure 6. Samples BH-145 and HC-3 lie beyond the limits of the section. bh = Bully Hill horizon; rs = Rising Star horizon
whereby elements inferred to have been immobile in the alteration reaction and the densities of unaltered protolith and altered products are used to calculate both the volume changes and elemental gains and losses accompanying alteration.

Two laboratories, XRAL and TML, provided the geochemical data. Several samples were analyzed by both labs to test for interlaboratory consistency. These sample analyses are consistent for all components except TiO₂, in which TML results are systematically lower than the XRAL analyses. This difference is noted and accounted for where appropriate in the following discussion.

Application of Gresens Method

Unaltered Protolith. As evidenced by the Hughes plot (Figure 22) and the discussion of alteration (CHAPTER 3), there are no pristine, unaltered rocks in the Bully Hill area. Rocks demonstrated to be least-altered will therefore be used as standards to compare with the altered samples in the calculations.

BH-3, BH-145, and BH-232 are designated the least-altered standards in the mass balance calculations on the basis of the following criteria: (1) remoteness from mineralization; (2) lowest degree of alteration determined petrographically; (3) low loss-on-ignition values; (4) position within the igneous spectrum of Figure 22; and (5)
closest approach to the chemical composition of average rhyodacite and rhyolite (Table 3). Even these least-altered rocks have significantly higher SiO\textsubscript{2} and lower CaO contents than average rhyolites and rhyodacites.

Two least-altered standards are used in this analysis in order to account for the interlaboratory difference in the determination of TiO\textsubscript{2} (Table 3). Standard 1 uses the average TiO\textsubscript{2} values from XRAL for BH-3 and BH-145, and is used to evaluate reactions involving samples analyzed by XRAL. Standard 2 uses the average TiO\textsubscript{2} value determined by TML for BH-145 and BH-232, and is used in calculations involving samples analyzed by TML. All other components of both standards are the average of TML's BH-145 and BH-232 data and XRAL's data for BH-3 and BH-145.

**Immobile Elements.** Immobile components have constant ratios in variably-altered rocks of similar parentage, so that a graph of immobile versus immobile components will form a straight line that intersects the origin (Finlow-Bates and Stumpfl, 1981). The closeness of fit of data points to a 'best-fit' line which passes through the origin on a plot involving hypothesized immobile components is therefore a test of immobility.

TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Zr, Nb, and Y have behaved isochemically in some hydrothermal systems (e.g., Winchester and Floyd, 1977; Finlow-Bates and Stumpfl, 1981; and Costa, Barnett and Kerrich, 1983). Figure 26 presents plots that test the
Table 3. Chemical compositions of average unaltered andesite, rhyodacite and rhyolite, and of Bully Hill area standards (see text). (1) LeMaitre, 1976; (2) Chayes, 1969

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<th>Weight percent oxides</th>
<th>Parts per million</th>
<th>Spec.</th>
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<tr>
<td>B.H. AREA DATA</td>
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Ave. Dekkas       | 61.3 | 16.60 | 1.790 | 2.400 | 6.75 | 0.58 | 6.67 | 0.110 | 0.61 | 0.17 |
Standard 1        | 78.8 | 11.21 | 0.201 | 0.403 | 4.53 | 2.04 | 1.61 | 0.029 | 0.12 | 0.03 | 1.14 | 39 | 150 | 7 | 902 | 2.64 |
Standard 2        | 78.8 | 11.21 | 0.201 | 0.403 | 4.53 | 2.04 | 1.61 | 0.029 | 0.08 | 1.14 | 902 | 2.64 |
immobility of TiO₂, Al₂O₃, Zr, Nb, and Y in the lava unit suite. Zr, TiO₂, and Al₂O₃ appear to have behaved isochemically. Exceptions to this are BH-27 (the sample of Type 1 alteration) on the Zr-Al₂O₃ plot, suggesting Al mobility in this sample, and the scatter of data on the Al₂O₃-TiO₂ plot, which is largely due to the systematic laboratory differences in the determination of TiO₂.

Linear trends are evident in plots involving Nb, but the absolute concentrations of Nb in the samples (4 to 8 ppm) are too close to the detection limit of the analyses (2 ppm) for sufficient resolution of the data points. It is clear, however, that Nb was added in BH-27. Plots involving Y also show linear trends with a fair amount of scatter. Y was apparently somewhat mobile in the alteration reactions.

In summary, Zr and TiO₂ are considered to be immobile in all of the alteration reactions to be analyzed. Al₂O₃ is also considered immobile except in BH-27, the most extremely altered sample. Nb and Y were apparently mobile in at least the highly altered samples, and therefore will not be considered to be immobile in any reaction. These conclusions are similar to those of Finlow-Bates and Stumpfl (1981), who summarized data from five volcanogenic massive sulfide deposits and found Zr and TiO₂ to have been immobile during intense hydrothermal alteration, while Nb and Y were in some cases extremely mobile.
Figure 26 a-j. Plots of: a. TiO$_2$ versus Al$_2$O$_3$; b. Zr versus TiO$_2$; c. Al$_2$O$_3$ versus Zr; d. Al$_2$O$_3$ versus Nb; e. TiO$_2$ versus Nb; f. Zr versus Nb; g. Y versus Nb; h. Y versus Zr; i. Al$_2$O$_3$ versus Y; and j. TiO$_2$ versus Y for lava unit samples. Figures a-c also show average igneous compositions (Al$_2$O$_3$ from LeMaitre, 1976; TiO$_2$ and Zr from Winchester and Floyd, 1977) and differentiation trends. AND = andesite; D-RD = dacite –rhyodacite; RHY = rhyolite
Figure 26, continued.
Figure 26, continued.
Igneous differentiation trends showing the average concentrations of TiO₂, Zr, and Al₂O₃ in andesites, dacite/rhyodacites, and rhyolites from LeMaitre (1976) are superimposed upon the plots in Figure 26a-c. The following conclusions may be derived from these graphs: (1) the immobile element signatures of the lava unit suggest a bulk composition of rhyolite; (2) the trend of the data points from Type 1 alteration through least altered samples along the 'best-fit' lines represents a trend from most- to least-altered rocks, in a sequence that agrees with field and petrographic observations; (3) this alteration trend is a dilution trend, since the concentrations of immobile elements in all altered samples are less than those of the least-altered samples; and (4) even the least-altered samples have diluted immobile element concentrations relative to average igneous values.

Mass Balance Calculations. The graphical means of presenting Gresens' (1967) method presented by Grant (1986) is used in this discussion (Figure 27). In these isocon diagrams, the chemical components of an altered sample are plotted against the average concentrations of the least-altered standards, and the alteration reaction which produced the altered product from the least-altered standard can be examined. Concentrations of the chemical components may be multiplied by arbitrary factors to facilitate the use of the isocon diagrams.
Figure 27a. Quartz keratophyre sample versus standard 1.

Figure 27a-f. Isocon diagrams (Grant, 1986) of lava unit samples. Solid lines = immobile element isocons.
Figure 27b. Type 1 alteration versus standard 1. Dashed line = constant volume isocon

Figure 27c. Average of two samples of Type 1 alteration versus standard 2.
Figure 27d. Type 2 alteration versus standard 1.

Figure 27e. Type 2 alteration versus standard 2.
Figure 27f. Type 3 alteration versus standard 2.
On an isocon diagram, a line, called an isocon, is drawn through the origin and components considered to be immobile in the alteration reaction being considered. Components which lie above the isocon line have been added to the altered sample during the alteration reaction, while those lying below the isocon line have been subtracted. The percentage gain or loss of any component can be calculated graphically using the intersection of a line defined by the component and the origin with a vertical scale constructed on the graph (Figure 27a). The slope of the isocon line is used to calculate mass and (if density data are available) volume changes in the alteration reaction.

An isocon drawn on the basis of constant volume is also shown on Figure 27b. Since differences in density between the altered samples and standards are small in every reaction examined, constant mass isocons are virtually identical to constant volume isocons.

Results

Both keratophyrization, represented by BH-58, and the relatively high temperature hydrothermal alteration associated with the Bully Hill-Rising Star mineralization are evaluated. Although the sample coverage is far from comprehensive, important chemical changes are indicated from the data. Figure 28 presents the percent gains and losses
derived by the Gresens analysis of some of the chemical components on reconstructed cross-sections.

**Keratophyrization.** The most significant chemical changes in BH-58 are an essentially complete loss of $K_2O$ and a 50% gain of $Na_2O$. This roughly corresponds to a 1:1 replacement of $K$ by $Na$, the dominant process of keratophyrization (Hughes, 1972). Mineralogically this is represented by the albitization of igneous potassium feldspars. The loss of 20% $CaO$ from BH-58 also distinguishes it from the high temperature hydrothermal suite, which is characterized by almost total loss of $CaO$.

Significant quantities of $MgO$, $MnO$, and $Fe_2O_3$ have also been removed from the sample, and may represent overprinting of the high temperature hydrothermal event.

**Bully Hill-Rising Star Alteration Zone.** Silicification is the dominant process of the hydrothermal system in the Bully Hill-Rising Star mine area, affecting all altered rocks. Gains in $SiO_2$ range from up to 250% in Type 1 alteration zones to about 20% in Type 3 zones. $SiO_2$ gains have a direct positive correlation with degree of alteration in the high-temperature alteration suite.

$K_2O$ additions of up to 60% occur in samples from alteration Types 1 and 2. Although the bulk of Type 3 alteration would probably also show $K_2O$ additions, sample BH-234 is depleted in $K_2O$ relative to the standards. This
Figure 28a-d. Schematic cross-sections showing percent gain or loss of chemical components from altered samples of the lava unit, calculated from data compiled in Figure 27. For sample numbers, refer to Figure 25.
28b. Percent loss or gain of CaO (top) and Na₂O (bottom).

28c. Percent loss or gain of K₂O.
28d. Percent loss or gain of MgO (top) and Fe₂O₃* (bottom).
is because sericitization in BH-234 is not as prominent as in most rocks from Type 3 zones.

Na$_2$O is essentially completely leached in alteration Types 1 and 2. BH-234 is depleted by 50%, suggesting that a halo of decreasing Na depletion surrounds the footwall area of the mineralizing systems.

CaO is essentially totally removed in all samples except BH-27 and BH-234. In these latter samples, the presence of CaO is due to carbonate alteration.

Fe$_2$O$_3$ has been removed from all of the footwall rocks sampled, except for BH-27, with relative depletions decreasing away from the orebodies. The 60% gain in BH-27 is due to the presence of iron-rich carbonate alteration and quartz-pyrite veinlets.

With the exception of BH-27, MgO has been added to the altered rocks in increasing amounts with increasing distance from the orebodies. MgO has been depleted by 20% in BH-27.

In the Bully Hill area, barite occurrence provides an excellent guide to proximity to syngenetic horizons, even in areas distal to known massive sulfide mineralization. For example, BH-36 and BH-37 cannot be identified as anomalously altered or mineralized on the basis of major element chemistry (see Figure 2 and following discussion of alteration index), but their Ba contents (>1000 ppm) are highly anomalous with respect to other Bully Hill area samples.
The anomalous Ba contents can be related to their proximity to the Bully Hill-Copper City horizon (Figure 2). Within the lava unit, large additions of Ba occur in all samples of Type 1 alteration and in the sample of Type 2 alteration which is proximal to the Bully Hill horizon. BH-63b is a highly altered lava from a Type 2 zone relatively distal from the Bully Hill horizon, and actually shows a Ba depletion. The approximately 100% gain in Ba in BH-234 is consistent with its location close to the projection of the Rising Star horizon.

Gains in volume occur in all of the altered rocks. Volume additions range from 200% in the most-altered Type 1 zones to 10% in the sample of Type 3 alteration. As is the case with SiO₂ and L.O.I. gains, the magnitude of volume gains has a direct positive correlation with degree of hydrothermal alteration.

The volume gains in Type 1 alteration range from 100 to 200%. Additions of this magnitude were largely the result of extensional fracturing and subsequent infilling with quartz veinlets. Type 1 zones developed immediately below the sea water/sea floor interface, which would allow essentially unlimited extension. The volume additions of 30-70% indicated for the samples of Type 2 alteration are, however, surprisingly high. These results are merely a quantification of the dilution trends indicated on Figure 26. Since only very small changes in density accompanied
the alteration reactions, the hydrothermal additions that caused the dilution were taken up almost exclusively by increases in volume.

Constant volume isocons can be used to test the alternative hypothesis of constant volume reactions. The constant volume isocon on Figure 27b demonstrates that a constant volume assumption is untenable in the case of BH-27. For example, a gain of only 15% SiO₂ is indicated in this sample, which is essentially completely silicified (93.3 wt.% SiO₂). Large depletions in TiO₂, Al₂O₃, and Zr are indicated in all of the samples under the assumption of constant volume. Because these components have constant ratios in the alteration reactions, the magnitude of the depletions are identical in each reaction considered. Since these components occur in a wide variety of mineral phases (Ti in biotite and sphene, Al in feldspar and chlorite, Zr in zircon and allophane), it is highly unlikely that each element would be leached in exactly the same proportion.

**Elemental Changes in the Dekkas Andesite**

SiO₂ additions to lava unit samples in the Bully Hill-Rising Star mine area are uniformly high. Smaller silica additions in areas distal to massive sulfide mineralization are evidenced by the common presence of groundmass replacement by fine-grained quartz in samples of Type 7 alteration. Taken as a whole, huge additions of silica are
necessary to account for the extensive silicification of the Bully Hill rhyolite in the Bully Hill area. The Dekkas andesite underlying the Bully Hill rhyolite in the Bully Hill area is highly altered, and is a potential source of the silica.

In order to evaluate elemental gains and losses in the Dekkas andesite, four of the five samples of the Dekkas andesite that plot within the andesite field on Figure 24 (HC-8, HC-10, SH-33, and SH-34) were averaged and plotted against a standard consisting of an average andesite composition (Table 3; Figure 29). The fifth sample of the Dekkas andesite (SH-30) was excluded because of its anomalously high SiO₂ contents and position close to the rhyodacite/dacite field of Figure 24. Since the andesite standard is not necessarily representative of the composition of unaltered comagmatic Dekkas andesite, the results can only be applied in a qualitative manner.

Two isocons are shown on Figure 29, one constructed on the basis of TiO₂ immobility and the other on the basis of Al₂O₃ immobility. The reason these components do not lie on a single isocon is probably that the samples of Dekkas andesite are not comagmatic with the average unaltered andesite standard, so that primary compositional distinctions between the Dekkas andesite and the standard are evident. Results from Figure 29 must therefore be treated qualitatively.
Figure 29. Isocon diagram of Dekkas andesite average versus andesite standard.

Figure 30. Isocon diagram of cleavage domain (63a) versus lithon domain (63b).
Keratophyrization of the andesite samples is evident from the large addition of $\text{Na}_2\text{O}$ and depletion of $\text{K}_2\text{O}$; the significant depletion of $\text{CaO}$ is probably a manifestation of the hydrothermal system which formed the Bully Hill-Rising Star orebodies.

Regardless of which isocon is chosen, $\text{SiO}_2$ has not been leached from the Dekkas andesite. It is likely that $\text{SiO}_2$ has actually been added to the samples of the Dekkas andesite. The andesites lying beneath the Bully Hill rhyolite in the Bully Hill area do not appear to be a viable source of silica for the overlying felsic rocks.

**Alteration Index**

The following is an index which can be used with whole rock data to estimate the degree of ore-related hydrothermal alteration, and hence proximity to ore, in felsic rocks of the Bully Hill area:

$$(\text{K}_2\text{O} + \text{SiO}_2/20)100/(\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{SiO}_2/20)$$

adapted from the index of Ishikawa et al. (1976) for the Kuroko district. This index ranks alteration by the degree of silicification and sericitization and the magnitude of $\text{CaO}$ and $\text{Na}_2\text{O}$ depletions. Since $\text{MgO}$ additions within altered rocks increase with distance from the ore horizons, placement of $\text{MgO}$ in the denominator serves to differentiate samples within altered zones.
Figure 31 is a map of alteration indices in the Bully Hill area. Indices below 45 generally identify quartz keratophyres, although rocks with significant carbonate alteration are also included in this range. Relatively unaltered samples lie in the range 45-55. Samples with indices >55 define the limits of the visually-obvious hydrothermal alteration zone in the Bully Hill-Rising Star mine area, with values in the 95-100 range restricted to samples from Type 1 alteration zones.

Chemical Changes Accompanying Spaced Cleavage Formation

Spaced cleavage forms by the process of pressure solution. Mobile components, such as quartz and calcite, are removed and relatively immobile components, such as clay minerals, chlorite, and micas, are residually concentrated (Ramsay, 1980). A Gresens analysis is used to determine the mobility of chemical components during formation of the solution cleavage in the lava unit. The alteration reaction examined is the change from unfoliated rock (lithon domain) to foliated rock (cleavage domain) during pressure solution, a process which postdated hydrothermal alteration of the rocks. The analysis is valid only if the system was open, and all components removed during formation of the cleavage domain were lost from the system.

A sample of a cleavage domain and one from the lithon domain immediately adjacent to it are presented on an
Figure 31. Alteration Indices (A.I.) of felsic volcanic rocks from the Bully Hill rhyolite and Pit formation plotted on a map showing the Bully Hill-Copper City and Rising Star mineralized horizons. Outline encloses area of A.I. > 55. See text for explanation of A.I.
isocon diagram in Figure 30. TiO₂ and Al₂O₃ lie along a line which intersects the origin, so these components are assumed to have behaved isochemically during cleavage formation. The isocon indicates that 80% Fe₂O₃ *, 55% K₂O and 25% Na₂O have been added to the cleavage domain, while 40% SiO₂ and 25% MgO were removed. Although Ba remained immobile in this reaction, barite was remobilized into cleavage domains in other areas. A volume loss (equal to loss of mass) of about 30% accompanied cleavage formation, which is consistent with other data from solution cleavage studies (Groshong, 1988).

The Fe₂O₃ * increase is due to the supergene enrichment of hematite in the cleavage domains of the sample. The K₂O and Na₂O increases indicate that these components were not only residually enriched, but were also added to the cleavage domain by the fluids involved in the solution process. These components are present as K-Na clays and micas in the cleavage domain.
CHAPTER 8

ORE PETROLOGY

Introduction

Eight polished thin-sections of sulfide-rich syn­
genetic mineralization and one of an epigenetic vein were examined in both transmitted and reflected light. The syngenetic samples were taken from dumps from underground workings in the Bully Hill (BH-300 and BH-500), Rising Star (BH-251 and BH-252), and Copper City (CC-37, CC-30-1 and CCD-2) mine areas, and from a dump to the prospect located one kilometer west-southwest of the Copper City mine (SH-45). The samples were selected to represent diverse types of mineralization, but are more representative of what was waste rock (relatively sphalerite-rich) than what was ore (relatively copper-rich) at the time the mines were in production. The epigenetic samples (BH-61) came from a dump at an adit that explores a vein on the southwest slope of Bully Hill (Figure 21).

One dump sample from the Copper City mine area (CC-30-1) is made up of a breccia of mudstone fragments. Sul­fide-sulfate mineralization partially replaces the fragments and fills open spaces between them. This sample is clas­sified as syngenetic ore since the first occurrence of mud­
stone in the area is along or immediately above the Copper City horizon, and the mineralization has parageneses and textures identical with those of the other syngenetic ore samples.

Paragenetic relationships in the syngenetic samples are consistent and have led to the delineation of four stages of mineralization (Stages 1 through 4, below) defined by mineral assemblages of similar paragenesis and texture (Figure 32). Several of the stages are represented in each polished section, with one stage usually predominating.

Mineral abundances in six of the syngenetic samples are grossly similar, with sphalerite ≈ barite > pyrite > galena > chalcopyrite > tetrahedrite-tennantite >>> bornite > pyrrhotite. These mineral proportions correspond to massive black or semiblack ore of the Kuroko district (Eldridge, Barton and Ohmoto, 1983). The seventh specimen (CCD-2) contains pyrite > chalcopyrite > sphalerite > barite, which is grossly similar to powdery yellow ore of Kuroko. Quartz, chlorite, sericite, calcite, and anhydrite are additional gangue minerals which occur in variable quantities in the specimens examined. The epigenetic vein sample contains barite > sphalerite > chalcopyrite > pyrite >> tetrahedrite-tennantite >> bornite.
Figure 32. Paragenetic sequence of Stages 1 to 4 in syngenetic sulfide-sulfate mineralization.
Mineral Paragenesis and Textures

Syngenetic Mineralization

Stage 1. Stage 1 ore is characterized by banded fine-grained pyrite + sphalerite ± gangue (Figure 33). Stage 1 is similar to Kuroko ores classified as facies 1 by Eldridge et al. (1983) and primitive ore by Barton (1978). Pyrite occurs as fine-grained (usually ≤25 μm) framboids, cubes and colloform growths (Figures 34 and 35). Some colloform masses are up to 2 mm in the longest dimension. Sphalerite occurs in polycrystalline anhedral masses which are identified as Stage 1 mineralization by their conformable interlayering with Stage 1 pyrite bands and absence of open space crystalline growth. Stage 1 gangue minerals include fine-grained to cryptocrystalline barite, quartz, Mg-rich chlorite, anhydrite and sericite.

Galena and tetrahedrite-tennantite occur in minor amounts as irregular patches and blebs within Stage 2 sphalerite interpreted to be recrystallized Stage 1 sphalerite (see below), and rarely as layers within colloform pyrite in cases where a replacement origin or coexistence could not be determined. These occurrences may represent additional Stage 1 mineralization. No evidence of Stage 1 chalcopyrite was observed.

Stage 2. Stage 2 mineralization is divided into two substages, Stage 2a and Stage 2b. Stage 2b ore is distin-
Figure 33. Banded Stage 1 pyrite and sphalerite ore. Sample SH-45.

Figure 34. Photomicrograph of Stage 1 colloform pyrite (dull grey) in quartz gangue (white), in partial reflected and transmitted plane-polarized light. Colloform masses are broken and connected by quartz crystal fibers. Width of field is 0.7 mm. Sample SH-45.
guished from Stage 2a ore by larger grain size and greater development of chalcopyrite disease in sphalerite.

Sphalerite and pyrite dominate Stage 2a mineralization; barite is less common. These minerals occur as recrystallized Stage 1 phases and as coarse-grained (commonly 0.1 to 1 mm) subhedral- to euhedral-terminated crystals lining former cavities within masses of recrystallized Stage 1 mineralization (Figure 36). Stage 2a minerals fill irregularly-shaped vein-like openings, tubular channels and vugs. Stage 2a is similar to facies 2 mineralization of Eldridge et al. (1983).

Stage 2a pyrite is commonly formed by the recrystallization of fine-grained colloform pyrite of Stage 1 into euhedral cubes. In areas where Stage 1 pyrite was abundant, adjacent cubes may coalesce into larger cubes (Figure 37). In some cases, partial replacement of Stage 2a cubic pyrite by later sulfides creates atoll textures which reveal cores of fine-grained Stage 1 colloform pyrite. Microprobe scans of several Stage 2a pyrites using energy dispersive analysis revealed the presence of gold.

Stage 2a pyrite typically contains inclusions of other sulfide minerals. Sphalerite inclusions are most common, but all of the hypogene sulfide minerals listed above are represented as inclusions. Inclusions within Stage 2a pyrite represent the sole occurrence of pyrrhotite and the predominant occurrence of bornite in the sections
examined. Included blebs of sphalerite, tetrahedrite-tennantite, galena and chalcopyrite may have formed predominantly by trapping of adjacent phases during the recrystallization of Stage 1 pyrite, although a replacement origin cannot be ruled out in most cases. Bornite and chalcopyrite commonly occur together in single inclusions, suggesting that bornite is the product of a reaction between the host pyrite and included chalcopyrite.

The size of anhedral sphalerite crystals within recrystallized masses of Stage 1 sphalerite is determined by examination of cleavage traces and crystallographically-oriented chalcopyrite disease. Stage 2a sphalerite has weakly-developed chalcopyrite disease and contains less than 0.001 mole percent FeS (see below). Stage 2a sphalerite replaces Stage 2a pyrite in some cases, and shows mutual boundary relationships in other cases.

Stage 2a barite occurs as patches of anhedral to subhedral crystals of recrystallized Stage 1 barite and as subhedral to euhedral open space-filling laths. Cavity-filling barite may in part be younger than the open space-filling Stage 2a sphalerite and pyrite.

Although crude banding is commonly discernible in hand specimen and/or thin-section in samples dominated by Stage 2a mineralization, it is a remnant Stage 1 texture which is variably preserved during Stage 2a recrystallization. These bands vary from alternating millimeter-scale
Figure 35. Photomicrograph of Stage 1 framboidal pyrite (white) in quartz gangue (dark grey), in reflected light. Some framboids show partial recrystallization into masses of fine-grained pyrite cubes. Width of field is 0.18 mm. Sample SH-45.
pyrite-rich and sphalerite-rich layers to thin, discontinuous layers of fine-grained cubic and colloform pyrite within recrystallized sphalerite-rich masses. Weakly defined layers of coarsely-crystalline cubic pyrite within sphalerite masses less-commonly preserve Stage 1 banding.

Mineralization which cross-cuts Stage 2a is characteristically restricted to Stage 3a (see below), so that chalcopyrite contents of samples dominated by Stage 2a mineralization are low and galena contents are relatively high.

Stage 2b is characterized by large, equant, growth-zoned sphalerite crystals up to 3 mm in diameter and 1 to 2 mm pyrite cubes. In addition to their exceptional size, Stage 2b sphalerite crystals are extensively attacked by chalcopyrite disease and contain 0.005 to 0.012 mole percent FeS. Stage 2b mineralization does not coexist with Stages 1 and 2 in the specimens examined, but is characteristically overprinted by chalcopyrite-rich Stage 3b mineralization. Banding is not present in samples dominated by Stage 2b mineralization. Stage 2b is equivalent to coarse-grained facies 2 of Eldridge et al. (1983).

Stage 3. Chalcopyrite characterizes Stage 3 mineralization, which is subdivided into Stages 3a and 3b. Galena and tetrahedrite-tennantite occur in the relatively chalcopyrite-poor Stage 3a ore, while Stage 3b ore is dominated by chalcopyrite.
Stage 3a mineralization is dominated by open-space filling galena and subordinate amounts of tetrahedrite-tennantite and chalcopyrite. Stage 3a ore cross-cuts Stage 2a mineralization, infills the remaining voids into which Stage 2a crystals projected, and partially replaces all minerals from the previous two stages. Euhedral crystals of Stage 2a pyrite and sphalerite are commonly rounded when in contact with Stage 3a minerals (Figure 36). Stage 3a minerals replace Stage 2a minerals along grain boundaries and fill preexisting fractures in Stage 2 minerals (Figure 36). Stage 3a has no counterpart in the classification of Kuroko ores by Eldridge et al. (1983).

Tetrahedrite-tennantite is closely associated with Stage 3a galena. Both mutual boundary relationships between the minerals and textures suggestive of galena replacement of tetrahedrite-tennantite are common; textures indicating tetrahedrite-tennantite replacement of galena are least common.

Stage 3a chalcopyrite has both mutual boundary relationships with galena and tetrahedrite-tennantite in some cases and replacement textures in other cases. Regardless of its paragenetic relationship with Stage 3a galena and tetrahedrite-tennantite, Stage 3a chalcopyrite is clearly associated with these minerals. Stage 3a chalcopyrite replaces all Stage 1 and 2 phases, and is probably present
as the weakly-developed chalcopyrite disease in Stage 2a sphalerite.

Stage 3b mineralization is dominated by chalcopyrite, which replaces all previous sulfide mineralization. Coarsely-crystalline pyrite appears to be closely associated with Stage 3b chalcopyrite in some specimens, but the chalcopyrite replaces this pyrite in all cases. Stage 3b chalcopyrite characteristically replaces Stage 2b sphalerite and pyrite, and rarely cross-cuts ore dominated by Stage 1 or 2a mineralization. Advanced chalcopyrite disease in Stage 2b sphalerite is locally seen to pervade its host from fractures filled by Stage 3b chalcopyrite, suggesting that the high degree of chalcopyrite disease in Stage 2b sphalerite is a manifestation of Stage 3b mineralization. Stage 3b is similar to facies 3 of Eldridge et al. (1983).

Stage 4. Barite, with or without trace quartz and calcite, is the latest stage of mineralization and most common type of barite in the sections examined. Stage 4 barite is most abundant in samples characterized by Stages 2a and 3a mineralization, and significantly dilutes the base metal contents of these samples in many cases. Stage 4 barite is a minor constituent of samples dominated by Stages 2b and 3b.

Voids filled by Stage 4 barite formed when fluids undersaturated with respect to all sulfide minerals eroded channels and vugs in the ores. Barite was precipitated as
laths, which occasionally occur in fan-shaped aggregates, and in masses of anhedral crystals. Sphalerite was dissolved preferentially over galena, pyrite and chalcopyrite (Figure 38). In cases of advanced dissolution, a sponge-like mesh of sphalerite and Stage 2a cavity-filling mineralization is filled with Stage 4 barite. Eldridge et al. (1983) do not identify a similar stage of mineralization in the Kuroko ores.

**Other Minerals.** Trace amounts of colorless fine-grained mica occur as subhedral to euhedral unoriented acicular crystals which cross-cut all sulfide and gangue minerals of the four stages of mineralization. It is interpreted to be a metamorphic phase.

Covellite is an uncommon mineral in the sections examined. It occurs as thin films along sulfide-gangue contacts and as replacements of chalcopyrite, galena and sphalerite. It is interpreted to be of supergene origin.

**Syndepositional Textures.** Clastic textures are common in many of the specimens examined. Clasts of various stages of mineralization, as well as massive syngenetic barite and lithic fragments, commonly occur within single thin-sections (Figure 39). Ore samples may be entirely clastic, or may have been mineralized subsequent to incorporation of the clasts.

Crystal fiber growths of quartz, barite and calcite are occasionally developed adjacent to extended sulfide-rich
Figure 36. Photomicrograph of subhedral void-filling Stage 2a sphalerite (brown-grey) and pyrite (white), infilled and partially replaced by Stage 3a galena (grey-white), tetrahedrite-tennantite (light grey) and chalcopyrite (off-white), in reflected light. Note rounding of sphalerite and pyrite euhedra, fracture filling of galena in sphalerite in center of photo, and mutual boundary of tetrahedrite-tennantite and galena at bottom left corner. Width of view is 0.18 mm. Sample BH-251.
masses (Figure 34), usually along planes developed at high angles to Stage 1 layering. These extensional features are in many cases cross-cut by late-stage mineralization, and are interpreted to be related to the slumping events which formed the clastic ores.

These clastic and extensional textures suggest that sulfide rich accumulations on the seafloor were commonly transported and redeposited. Clastic textures are quite common in Kuroko ores (e.g., Barton, 1978; Eldridge et al., 1983).

**Epigenetic Mineralization**

The single vein sample studied is from a dump to a small prospect on a vein in the footwall of the Bully Hill horizon, distal to the Bully Hill mine orebodies. In this sample, the earliest phase is fine-grained (≤50 µm) cubic pyrite. The cubic phase is overgrown by coarsely-crystalline pyritohedral pyrite. Chalcopyrite, which is relatively abundant in this sample, preferentially replaces the pyritohedral pyrite, exposing the cubic cores. Sphalerite, which does not exhibit chalcopyrite disease, replaces the chalcopyrite and both stages of pyrite. Late-stage coarsely crystalline barite replaces all of the sulfide minerals. Small amounts of galena and tetrahedrite also occur in the sample, but their position in the paragenetic sequence is uncertain.
It is interpreted that the epigenetic mineralization can be correlated with the syngenetic paragenesis outlined above. The fine-grained and coarse-grained pyrite phases may represent Stage 2a and Stage 2b, respectively. The chalcopyrite and barite are likely representative of Stage 3b and Stage 4, respectively.

Model of Orebody Evolution

On the basis of ore textures in the Hokuroku district, Eldridge et al. (1983) defined three ore facies (facies 1, 2 and 3) and proposed a model for the evolution of the massive sulfide bodies. These facies are commonly deposited in ascending numerical sequence at any point within the sulfide mound, but in some specimens the sequence is repeated. Since they considered that all of the facies were deposited synchronously in different portions of the mound, the term facies was chosen instead of stage. Their basic model for the formation of the three facies is summarized below.

Facies 1 mineralization forms when metal-bearing hydrothermal solutions exhale into and mix with cold seawater. This results in rapid precipitation of fine-grained, commonly colloform sulfides and gangue. As wallrock temperature increases in the footwall of the sulfide pile, the temperature of discharging fluids increases. Facies 1 minerals exposed to the high temperature solutions are dis-
Figure 37. Photomicrograph showing recrystallization of Stage 1 pyrite framboids into Stage 2a crystalline pyrite (white) within Stage 2a sphalerite (grey), in reflected light. Width of view is 0.18 mm. Sample BH-300.

Figure 38. Photomicrograph of framboidal pyrite (highly reflective) replaced by Stage 4 barite (grey), in reflected light. Preexisting sphalerite was completely replaced. Width of view is 0.18 mm. Sample BH-500.
solved and reprecipitated as coarse-grained facies 2 minerals. Facies 1 minerals continue to precipitate in the outer portions of the growing mound. Further increases in temperature of the hydrothermal fluids discharging into the mound result in the replacement of lowermost portions by facies 3 chalcopyrite, and the migration of facies 2 and 1 mineralization outward in the pile. These mound-building processes produce: the observed zoning of zinc-rich over copper-rich ore; the downward increase in grain size, which reflects both increasing proportion of facies 2 to facies 1 minerals and increase in size of facies 2 crystals; the downward increase in abundance of vug-filling crystals; and the downward increase in degree of chalcopyrite disease in sphalerite.

Ore textures in the Bully Hill area closely resemble those of the Hokuroku district. The three stages of mineralization described above are largely equivalent to the three facies of Eldridge et al. (1983), and probably formed in a similar manner. The model proposed by Eldridge et al. (1983) is considered to be applicable to the Bully Hill area ores, with a few minor additions.

The banding typical of Stage 1 ore may have formed by sequential sedimentary deposition of minerals from particulate suspensions in mixed fluids above the seafloor. Although Eldridge et al. (1983) suggest that growth of the mound was achieved primarily through facies 1 deposition, it
is unlikely that this would have been an efficient mound-building process owing to the likely loss of metals from dispersion into the ocean.

When the sedimentary accumulations were extensive enough to blanket areas venting the hydrothermal solutions, some of the Stage 1 mineralization would be directly exposed to high temperature hydrothermal exhalations and the formation of Stage 2a mineralization would ensue. A rind of anhydrite probably covered the growing mound, as proposed by Franklin (1986). Growth of the sulfide mound could now be accomplished by Stage 2a open space-filling of cavities dissolved in Stage 1 mineralization, replacement of anhydrite rind by Stage 2a minerals and continued settling of Stage 1 mineralization on top of the pile. Precipitation of Stage 2a minerals could result from mixing of hydrothermal fluids with warmed seawater, which would probably infiltrate the mound. Stage 2b mineralization, represented by coarse-grained pyrite and highly chalcopyrite diseased sphalerite, probably formed at the lowermost portion of the area characterized by the Stage 2 assemblage.

Stage 3a mineralization is relatively chalcopyrite-poor compared with Stage 3b. The Stage 3a assemblage formed within areas dominated by Stage 2a mineralization, in the mid to upper portions of the mound, from solutions which had already deposited much of their copper as Stage 3b (facies 3) mineralization.
In the waning stages of the hydrothermal system, the exhaling fluids became undersaturated in all of the sulfide minerals due to decreases in temperature. The low temperature solutions eroded channels in the sulfides throughout the mound and eventually deposited the late-stage barite. The collapse of the hydrothermal system into the Type 1 footwall zones may have brought about deposition of much of the late epigenetic barite as well.

The sequence of mineralization in the epigenetic vein sample represents peak hydrothermal mineralization overprinted by a retrograde hydrothermal assemblage. During prograde development of the deposit, Stage 2b pyrite is replaced by Stage 3b chalcopyrite. Subsequent collapse of the hydrothermal system, with associated decrease in temperature, resulted in retrogressive replacement of Stage 3b chalcopyrite and earlier pyrite by sphalerite, and eventually all sulfides by Stage 4 barite. The formation of a sulfide retrograde assemblage may be due to the insulating effect of the wallrocks, which would allow cooling of the hydrothermal system to occur gradually. Within the mound, however, infiltrating seawater could quickly dominate the less-vigorous introductions of relatively cool hydrothermal solutions, resulting in dramatic temperature reduction.
Figure 39. Photomicrograph of clastic ore, in plane-polarized transmitted light. Dark clasts are single crystals of Stage 2b sphalerite and pyrite. Light clasts are rock fragments and coarsely crystalline barite. Width of view is 5.4 mm. Sample CC-37.
Geochemistry of Ore Formation

The evolution of a portion of the sulfide mound through Stages 2a, 2b, and 3a mineralization involves physicochemical changes which can be examined on a plot of $a_{\text{O}_2}$ versus $a_{\text{H}_2\text{S}}$ (Figure 40). Eastoe and Nelson (1988) constructed this plot in their evaluation of Afterthought area mineralization because many of the mineral-mineral equilibria do not depend on pH and the relative quantities of reduced and oxidized sulfur species are easily presented. Stage 1 mineralization cannot be represented on the plot since it formed by the quenching of hot metal-rich solutions by seawater, and therefore does not approach an equilibrium process. Stage 3b chalcopyrite and Stage 4 barite probably formed at temperatures significantly higher and lower, respectively, than that of Stages 2 and 3a, and therefore are also excluded from Figure 40.

The temperature of the system (250°C), the salinity of the hydrothermal solutions (0.8 molal NaCl) and a pressure sufficient to prevent boiling of these fluids (50 bars) were derived from sulfur isotope and fluid inclusion data presented in later chapters. The presence of sericite and lack of potassium feldspar and kaolinite in alteration assemblages in footwall rocks suggests the pH was between 3 and 6 at probable values of $a_{\text{H}^+}$ (Barton and Skinner, 1979, figure 8.6). A pH of 5 is used in Figure 40. The hydrothermal fluids are assumed to be saturated in pyrite in
Figure 40. Conditions of mineralization Stages 2a, 2b and 3a, shown on a log $a_{O_2}$ vs. log $a_{H_2S}$ diagram (modified from Eastoe and Nelson, 1988). Cross-hatched fields correspond to mineral assemblages ($2a_{sb} = $ Stage 2a sphalerite + barite; $2b_s = $ Stage 2b sphalerite; $3a_{CG} = $ Stage 3a chalcopyrite + galena).
order to calculate chalcopyrite, bornite, covellite and sphalerite-FeS equilibria (Ohmoto et al., 1983). On the basis of microprobe analyses, the mole per cent FeS in Stage 2a sphalerite is less than $10^{-3}$ ($10^{-3.7}$ to $10^{-3.1}$), and ranges from $10^{-2.3}$ to $10^{-1.9}$ in Stage 2b sphalerite.

The temperature of formation of Stages 2b and 3a mineralization was probably somewhat higher than that of Stage 2a. The presence of galena and tetrahedrite-tennantite in the Stage 2b assemblage and the similar mineralogy of Stages 2a and 2b, however, suggest that the temperature differences are not significant for the purposes of the activity diagram. Thermochemical data are from Barner and Scheuerman (1978), except for data relating to aqueous chloride complexes of lead, zinc and barium (Ohmoto et al., 1983) and $\text{NaSO}_4^-$ (treated as in Ohmoto, 1972).

Standard states are as follows: pure crystalline substances at the pressure and temperature of interest for minerals; a hypothetical ideal 1 molal solution at the pressure and temperature of interest for dissolved species, including $\text{H}_2\text{S}$; and a hypothetical ideal gas at 1 bar and the temperature of interest for $\text{H}_2\text{O}$ gas. Activity coefficients were calculated with the modified Debye-Hückel equation of Helgeson (1969), assuming 90 per cent dissociation of NaCl. Values of $a$ were estimated from Garrels and Christ (1965, p. 62). Pressure corrections to equilibrium constants are assumed to be negligible.
On Figure 40, activity, molality, and $X_{FeS}$ contours are numbered in log units. Solid lines and $X_{FeS}$ contours are independent of pH; other lines are not. The $X_{FeS}$ contours give the FeS content of sphalerite in equilibrium with pyrite. The $X_{FeS}$ contours were calculated using an activity coefficient of 2.4 for FeS (Barton and Toulmin, 1966).

$NaSO_4^-$ is the predominant aqueous sulfate species under the specified conditions and therefore represents total aqueous sulfate. Lines representing $NaSO_4^-/H_2S$ molality ratios of 10, 1 and 0.1 are shown. The presence of significant syngenetic and epigenetic barites in Stages 1, 2a, and 4 with $\delta^{34}S$ values up to 12 per mil higher than contemporaneous seawater sulfate indicates that significant quantities of aqueous sulfate were supplied by the hydrothermal solutions (CHAPTER 10). It is therefore unlikely that hydrothermal fluids ever had $\Sigma SO_4^-$ contents significantly less than $10^{-5}$ m.

Stability fields corresponding to mineral assemblages of Stages 2a, 2b, and 3a mineralization, along with a suggested path of evolution of the hydrothermal fluids, are shown on Figure 40. The assumption that the total molality of all aqueous lead, zinc, barium, sulfate, and sulfide species in the hydrothermal fluids must exceed $10^{-5}$ prior to ore deposition in order to form significant concentrations of minerals containing these elements (Anderson, 1977) is used to limit the fields. The interpretation that $\Sigma SO_4^-$ did
not fall significantly below $10^{-5}$ m in Stages 2b and 3a places an additional constraint on these field boundaries; a limiting $SO_4^{2-}/H_2S$ ratio of 0.1 is selected.

Under the assumptions of constant temperature and equilibrium conditions, $a_{H_2S}$ and possibly the $SO_4^{2-}/H_2S$ ratio of the hydrothermal fluid decrease from Stage 2a to Stage 3a. The concentration of $H_2S$ in the hydrothermal fluid decreases from approximately $10^{-3.5}$ to between $10^{-4.5}$ and $10^{-5}$ molal, while $ESO_4^{2-}$ decreases from approximately $10^{-3}$ to between $10^{-5}$ and $10^{-6}$ molal along the path of fluid evolution. These changes are accompanied by constant to slightly decreasing $aO_2$.

Figure 40 suggests that the concentration of $ES$ in fluids which precipitated Stage 2a and 3a minerals was approximately $10^{-3}$ and $10^{-4.5}$ molal, respectively (aqueous sulfur concentrations less than $10^{-4.5}$ molal are probably insufficient to produce sulfide-sulfate orebodies). The field of Stage 2b mineralization is delimited by microprobe analyses of FeS contents in sphalerites from a single section. Sphalerites from samples of mineralization transitional to Stages 2a and 2b as described above would most likely occupy a field which spans the space between the fields of Stages 2a and 2b on Figure 40.

Stage 2a fluids have significantly greater aqueous sulfate and sulfide concentrations than Stage 3a fluids. If the model for the evolution of the sulfide mound of Eldridge
et al. (1983) is applicable to the Bully Hill area ore-bodies, each stage of mineralization was forming in different portions of the mound at the time Stage 3 mineralization began. In this model the path of fluid evolution shown on Figure 40, which would be reversed from the perspective of a fluid flowing from the base of the mound outward, must therefore be controlled by intramound processes, not by deep-seated evolution of the hydrothermal fluids. Intramound sources of sulfur include Stage 1 mineralization and seawater. Stage 1 mineralization that is dissolved by the high temperature solutions which ultimately precipitate Stage 2a ore could provide both $\text{H}_2\text{S}$ and $\text{SO}_4^{2-}$ to the hydrothermal fluids. Sulfate could also be supplied by seawater which infiltrates the sulfide pile, and could result in the interpreted increase in $\text{SO}_4^{2-}/\text{H}_2\text{S}$ ratios in Stage 2a fluids relative to Stage 3a fluids. Alternatively, the facies concept of Eldridge et al. (1983) is not rigidly applicable, at least to the specimens examined, and differences in sulfur concentrations were controlled by deep-seated processes within the hydrothermal system.
CHAPTER 9

FLUID INCLUSIONS

Introduction

Numerous samples of quartz and grey barite from epigenetic mineralization were collected for fluid inclusion study. Five of these samples, containing both quartz and barite, were prepared for analysis. Only two quartz samples (BH-10 and SH-41) contain primary fluid inclusions of sufficient size to be analyzed. Three of the barite samples (BH-10, BH-149 and SH-41) contain inclusions suitable for analysis.

The three samples analyzed are from Type 1 alteration zones. BH-10 is from the northern extension of the Rising Star mine mineralization and BH-149 is a sample of the Bully Hill mine stockwork zone. SH-41 is from the allochthonous block of intensely silicified mudstone which occurs within the megabreccia of the lower Pit formation southwest of the Copper City mine. The style of alteration and mineralization in this block is identical to that of Type 1 alteration zones associated with the Bully Hill, Rising Star and Copper City mines, but its point of origin is unknown.
The quartz in BH-10 consists of euhedral, growth-zoned crystals infilled by a later stage of interlocking anhedral crystals. Oxidized sulfide minerals are associated with the anhedral quartz stage. Fluid inclusions from the growth zones of the largest of the euhedral crystals were analyzed in detail; the anhedral quartz contains fluid inclusions which are too small for analysis. In SH-41, the quartz consists of numerous growth-zoned crystals lining a cavity in silicified mudstone.

The barite in all of the samples consists of aggregates of euhedral open-space-filling crystals. The barite is the youngest mineral phase in each of the samples, and partially replaces the earlier crystalline quartz.

**Analytical Methods**

Homogenization temperatures and freezing point depressions from approximately 150 fluid inclusions were measured (Figures 44 through 47). Uncertainties in temperature measurements are generally less than 5°C for homogenization temperatures and 0.1°C for freezing temperature determinations (±0.2 equivalent weight per cent NaCl; Potter et al., 1978). All homogenization temperatures are from inclusions which homogenized to the liquid phase. The small size of many of the fluid inclusions presented optical limitations which precluded measurement of both the filling temperature and salinity in every inclusion.
Figure 41. Isolated two phase primary-appearing fluid inclusion in quartz between planes of secondary inclusions, in plane-polarized transmitted light. Width of view is 0.18 mm. Sample BH-10.
Fluid inclusions larger than 15 μm in BH-10 quartz generally leak or decrepitate during heating runs, often before homogenization temperature is reached. In one case leaking could be attributed to tiny fractures present adjacent to the inclusion prior to heating. To circumvent this problem the sample was subdivided into many small chips, freezing temperatures were determined on selected inclusions from each chip, and then filling temperatures were determined on a limited number of the smaller inclusions (generally 2 to 8 μm). Vapor bubble sizes before and after the heating and freezing runs were carefully observed; filling temperatures were accepted only when they were reproducible and from inclusions which displayed no visible change in the size of the vapor bubble following the heating runs.

Nature of Inclusions

Fluid Inclusions

Planes of secondary fluid inclusions predominate in all of the samples examined (Figure 41). These planes commonly have irregular phase ratios ranging from all liquid to vapor-rich inclusions, but in general have liquid/(vapor + liquid) volume ratios greater than 0.5. Planes of secondary fluid inclusions which have little or no vapor phase at room temperature and show abundant evidence of necking down are common.
Primary-appearing fluid inclusions were selected on the basis of criteria outlined by Roedder (1984) (Figure 41). These inclusions range up to approximately 35 μm in the longest dimension. Most of the primary fluid inclusions identified have liquid/(vapor + liquid) volume ratios greater than 0.5 at room temperature.

Growth zones in the quartz of samples BH-10 and SH-41 occur as alternating clear and cloudy bands (Figure 42). The cloudy bands are delineated by dense concentrations of primary fluid inclusions, while the clear bands have relatively few fluid inclusions. In SH-41, two clear zones are separated by one fluid inclusion-rich zone. Quartz crystals in BH-10 contain seven well-defined inclusion-rich zones which separate eight inclusion-poor zones (Figure 42). These growth zones are numbered consecutively, with zones 1 and 15 representing the innermost and outermost zones, respectively. At high magnification the outermost zone can be subdivided into zones 15a and 15b.

Primary fluid inclusions in the fluid inclusion rich zones are irregularly shaped and usually less than 10 μm in the longest dimension. In SH-41, fluid inclusions in the inclusion-rich zone have highly irregular phase ratios, ranging from liquid-rich to vapor-rich.

In the eight clear growth zones in BH-10, primary fluid inclusions occur predominantly along growth lineations. These lineations lie perpendicular to the faces of
Figure 42. Growth-zoned quartz crystal utilized in fluid inclusion study, in plane-polarized transmitted light. Seven dark bands separate eight clear zones; zone 1 is the clear zone on the bottom left side, zone 6 is the thickest dark band and zone 15 is the wide clear band which rims the crystal. Width of view is 6 mm. Sample BH-10.
the crystal, and are defined by trains of prismatic primary fluid inclusions which are generally elongate in the lineation direction.

In the barites, most fluid inclusions are of indeterminate origin or are too small to analyze. Primary-appearing fluid inclusions in the barites have highly irregular liquid/vapor ratios. Wide ranges of filling temperatures from fluid inclusions in barite from Kuroko deposits have been reported, and are attributed to leakage, stretching and/or necking down of the inclusions (e.g., Tokunaga and Honma, 1974; and Pisutha-Arnond and Ohmoto, 1983). Bodnar and Bethke (1984) concluded that fluid inclusions in barite yield unreliable filling temperatures due to stretching of the inclusion walls, which may occur naturally or in the laboratory. Barite-hosted inclusions are also prone to necking down (Roedder, 1984). Since post-entrapment changes are indicated by the irregular phase ratios of barite-hosted fluid inclusions examined in this study, homogenization temperatures were not accepted as meaningful, and therefore are not evaluated.

Planes of pseudosecondary fluid inclusions occur in several growth zones in BH-10 quartz and in the inner zone of SH-41 quartz (Figure 43). No pseudosecondary inclusions were recognized in the barite samples.

In SH-41, liquid/(vapor + liquid) ratios of inclusions within single planes of pseudosecondary inclusions in
quartz range from 0.1 to 1.0. Halos of tiny fluid inclusions are visible around a few of these pseudosecondary inclusions, indicative of partial decrepitation (Lemmlein, 1956). No salinity data were obtained from the vapor-rich pseudosecondary fluid inclusions because an ice phase could not be recognized.

**Solid Inclusions and Trapped Salts**

A small percentage of primary fluid inclusions in zone 1 of BH-10 quartz contain relatively large, prismatic, birefringent salts of indeterminate composition. The large size of the salts relative to the host inclusions, and the presence of similar-appearing solid inclusions within the same zone suggest that the salts were trapped by the fluid inclusions. A few other fluid inclusions in this zone contain hair-like birefringent crystals which may be daughter salts. Sparse opaque solid inclusions are also present in BH-10 quartz.

The outermost clear zone of SH-41 quartz contains abundant, somewhat blocky birefringent solid inclusions with irregularly-rounded edges. The habit and birefringence of these solid inclusions are suggestive of barite.

Solid inclusions and apparent daughter salts in fluid inclusions are common in the barite samples. Up to three solid phases occur within a single fluid inclusion. The most common solid phase is highly birefringent and has a
platy, prismatic shape. These characteristics suggest that the solid may be anhydrite, which occurs extensively in the Bully Hill-Rising Star mine area. Volume ratios of this solid to the host inclusion are quite variable, and two crystals of the salt are present in some inclusions. This phase is also a common solid inclusion in the barite; in one crystal the solid inclusions define an apparent growth zone. These relationships suggest that the solid phases were trapped by the fluid inclusions, and therefore the presence of this salt is used as a criterion of primary origin of the host fluid inclusions (Roedder, 1984). At least two non-birefringent salts and one opaque phase of unknown composition also occur in fluid inclusions hosted by barite, and opaque solid inclusions are common.

A peculiar occurrence of the highly birefringent salt in barite is in fluid inclusions making up secondary or pseudosecondary planes. Two large crystals, relative to the size of the host inclusions, are commonly contained within each fluid inclusion in some of these planes, with each salt occupying an irregular, amoeboid extremity of the inclusion. These relationships suggest that these salts were trapped by the fluid inclusions.
Figure 43. Several planes of pseudosecondary fluid inclusions in quartz which terminate on a growth zone boundary (diffuse, dark vertical band on left side of photo), in plane-polarized transmitted light. Planes of pseudosecondary inclusions strike subhorizontally across the photo. Width of view is 0.18 mm. Sample SH-41.
Results

BH-10 and BH-149

Salinities of primary and pseudosecondary fluid inclusions in BH-10 quartz range from 3.5 to 6 equivalent weight percent NaCl, with a mean of 4.6 and a mode of 4.9 (Figure 44). There is a gradual increase in salinity from the core of the crystal to zone 15b, punctuated by anomalously high salinities from a plane of pseudosecondary inclusions that terminate at the top of zone 1, primary inclusions from the upper portion of zone 15a and an inclusion from a pseudosecondary plane which terminates at the top of zone 15a. Inclusions from the zone 1 pseudosecondary plane have a mean salinity of 5.3 equivalent weight percent NaCl. The zone 15a inclusions have the highest salinities recorded in BH-10 quartz, with a modal salinity value of 5.9 equivalent weight percent NaCl. The modal salinity value of zone 15b, which rims the quartz crystal, drops to 4.7 equivalent weight percent NaCl. Zone 6 is the only inclusion-rich zone for which data from primary inclusions were obtained.

The salinity values of the primary and pseudosecondary inclusions in BH-10 quartz are similar to or higher than average seawater salinity (≈3.5 equiv. wt % NaCl). Salinities of secondary fluid inclusions range to slightly lower values than primary inclusions (Figure 45).
Figure 44. Histogram of salinities of primary and pseudosecondary fluid inclusions from BH-10 quartz and barite from BH-10 and BH-149. Numbers in parentheses indicate growth zone. Data points for pseudosecondary inclusions are averages; numbers in brackets indicate the number of inclusions analyzed within each plane. SW = seawater
Figure 45. Histogram of salinities of secondary fluid inclusions in quartz. Data from individual planes are averaged.

Figure 46. Histogram of filling temperatures of primary, pseudosecondary and secondary fluid inclusions in BH-10 quartz. Arrows indicate minimum filling temperatures of primary inclusions (see text), and numbers within primary inclusion boxes and above arrows indicate growth zone. P1 = pseudosecondary inclusion from termination of zone 1.
The filling temperatures of primary and pseudosecondary fluid inclusions from zones 1 through 15a range from 240 to 260°C, with a mean of 248°C (Figure 46). Five additional fluid inclusions too small (≤2μm) to observe final homogenization yielded minimum filling temperatures ranging from 200 to 230°C. In these inclusions, the vapor bubble disappears into the dark borders of the inclusion well before homogenization is reached. These minimum temperatures are consistent with the homogenization data, and are considered significant because no inclusions of this size leaked during the heating and freezing runs. Fluid inclusions from zone 15b have a mean filling temperature of 186°C. While no change in filling temperatures accompanies the salinity increase from zones 1 to 15a, the limited data suggest that both filling temperatures and salinities decrease from zone 15a to 15b.

Two planes of secondary inclusions with consistent phase ratios in BH-10 were analyzed. The mean homogenization temperatures of the two planes are 158 and 170°C (Figure 46), and the salinity values of inclusions within these planes are close to the salinity of seawater.

The salinity values of primary fluid inclusions in the barites range from 4 to slightly more than 6 equivalent weight percent NaCl (Figure 44). Most of the primary inclusions did not freeze at temperatures as low as -110°C, however.
SH-41

Primary fluid inclusions in SH-41 quartz are restricted to the inclusion-rich growth zone. The four inclusions analyzed have salinity values ranging from 3 to 4.5 equivalent weight percent NaCl (Figure 47). Homogenization temperatures of three of these inclusions are 169, 171 and 189.5°C, although liquid/vapor ratios of primary fluid inclusions within this zone generally vary widely.

Salinities of pseudosecondary fluid inclusions in the quartz range from 2.6 to over 12 equivalent weight percent NaCl; all but one of the 27 inclusions analyzed have salinities equal to or greater than that of seawater (Figure 47). Some of the pseudosecondary inclusions do not freeze at temperatures as low as -110°C. Salinity values of inclusions within single pseudosecondary planes vary by as much as 4 equivalent weight percent NaCl. No pseudosecondary planes cross-cut the outermost clear zones, but in most cases it was not possible to determine if the pseudosecondary planes terminated at the top of the central clear zone or the top of the fluid inclusion-rich zone.

Salinities of a limited number of secondary fluid inclusions in SH-41 quartz range from 0 to over 5 equivalent weight percent NaCl (Figure 45). Liquid/vapor phase ratios of these inclusions are irregular. Several planes of inclusions in which a secondary or pseudosecondary habit could not be definitively assigned have salinity values ranging
Figure 47. Histogram of salinities of fluid inclusions from sample SH-41. p = primary inclusions; ps = pseudosecondary inclusions; s-ps = inclusions from secondary or pseudosecondary planes; SW = seawater; horizontal arrow indicates minimum salinity (see text).
from 0 to over 10 equivalent weight percent NaCl (Figure 47).

Only three primary fluid inclusions in SH-41 barite would freeze at temperatures as low as -110°C (Figure 47). Two have salinity values of approximately 10.5 equivalent weight percent NaCl. The third inclusion yielded only a minimum salinity estimate, 7.6 equivalent weight percent NaCl, owing to the metastable absence of a vapor phase at the temperature of melting (Roedder, 1984). These inclusions contain no daughter salts.

Interpretations

Evidence of Boiling

Evidence for or against boiling is important because boiling of hydrothermal fluids can cause ore deposition, and fluid inclusions that trap boiling fluids can lead to an accurate estimate of the pressure at the time of trapping. The fundamental evidence that fluid inclusions have trapped boiling fluids is the coexistence of vapor-rich, relatively low-salinity inclusions with liquid-rich, relatively high-salinity inclusions which homogenize to the vapor and liquid phase, respectively, at approximately the same temperature (Roedder, 1984).

In this study, evidence suggestive of boiling includes highly variable liquid/vapor ratios in primary and pseudosecondary fluid inclusions and the widely varying
salinities in the pseudosecondary inclusions in SH-41 quartz. The extreme range in salinity values, the fact that the variable salinities are all from liquid-rich inclusions and the evidence that at least some of the variability of phase ratios is due to partial decrepitation, all argue against boiling. Volatile loss during boiling due to decreasing pressure in a convective upflow leads to a relatively small salinity increase; a maximum increase in salinity of only about 30% results from the extreme example of adiabatic boiling and steam loss from 300°C to 100°C (Hedenquist and Henley, 1985). Boiling cannot solely account for the observed range in salinity. The variable phase ratios are probably due to one or more of the post-entrapment processes of partial decrepitation, leaking and necking down.

As is discussed below, episodic boiling could have produced the fluid inclusion-rich zones in the quartz samples. This possibility cannot be evaluated, and is not sufficient to prove that the hydrothermal solutions boiled.

Pressure Correction on Homogenization Temperatures

As there is no convincing evidence that the ore fluids boiled, the pressure in the Type 1 alteration zones during deposition of the quartz and barite must have exceeded the vapor pressure of the saline hydrothermal fluids at temperatures up to 250°C. This pressure can be estimat-
ed from the vapor-pressure curve of pure water since additions of NaCl in the amounts indicated from the fluid inclusion data result in negligible changes in the vapour-pressure curve (Roedder and Bodnar, 1980). Since Type 1 alteration zones formed at the seawater/seafloor interface, the pressure of the rock column was negligible and the total pressure can be assumed to have been from the overlying seawater column. In this case the minimum depth of seawater necessary to prevent boiling was approximately 400 meters (40 bars of water pressure).

Previous workers in the East Shasta area have suggested that the Late Permian volcanic arc was partly or intermittently emergent (Lapierre et al., 1986; Martin et al., 1985; and Albers and Robertson, 1961). Lapierre et al. (1986) concluded that the Nosoni, Dekkas, and Bully Hill formations were formed in a moderately deep to shallow submarine environment, with ignimbritic textures in some felsic volcanic rocks of the Nosoni formation suggesting that the volcanic arc was sometimes emergent. Geologic evidence from this study suggests that the Bully Hill rhyolite was erupted in a subaqueous environment.

Faunal evidence, including corals and fusulinids from small reefs preserved in shallow water limestone near the top of the Dekkas andesite in an area where the Bully Hill rhyolite is absent (Miller and Wright, 1987), and various neritic fauna represented in fossils throughout the
Pit formation (Albers and Robertson, 1961), suggests that shallow waters prevailed throughout much of the arc environment. The presence of vesicular igneous rocks in the Dekkas andesite, the upper mafic unit of the Bully Hill rhyolite and the mafic sills immediately overlying the Bully Hill mine horizon also indicate shallow water depths. It is likely that the Bully Hill area was submerged under less than 1000 meters of seawater when the orebodies formed. This depth corresponds to a pressure of about 100 bars.

Using a maximum depth of seawater of about 1000 meters, the maximum increase in homogenization temperatures due to the pressure correction is about 10°C (Potter, 1977). Since homogenization temperatures have an uncertainty of ± 5°C, the magnitude of the pressure correction is insignificant.

Discussion of Results

Samples BH-149 and BH-10 are from the Type 1 alteration zones associated with the Bully Hill and Rising Star mineralized horizons, respectively. Geologic and sulfur isotopic evidence suggests that the stockwork mineralization associated with the Type 1 zones is genetically related to the syngenetic orebodies of the mines.

Results from BH-10 quartz suggest that temperatures of the hydrothermal fluid in the stockwork zone immediately below the seafloor reached 250°C. The second stage of
quartz, from which no inclusions could be analyzed, is associated with sulfide minerals and may represent the main stage of mineralization. If this is the case, temperatures may have exceeded 250°C at the height of ore deposition.

Salinities indicated from BH-10 and BH-149 suggest that the hydrothermal solutions in the Rising Star and Bully Hill systems were similar to or higher than the salinity of unmodified seawater. The coincidence of the lower limit of hydrothermal salinities with seawater salinity suggests that seawater was an important component of the hydrothermal solutions.

As a component of the hydrothermal solutions seawater could be the source of the hydrothermal fluid, an endmember in a mixed hydrothermal solution, or a combination of these involving mixing of modified seawater solutions with cold seawater. With seawater as the source fluid, elevated salinities could result from reactions with country rocks at high temperatures in a convective hydrothermal system. Pisutha-Arnond and Ohmoto (1983), based on fluid inclusion and isotopic data from Kuroko deposits, proposed a model whereby consumption of water from an evolving seawater solution during the formation of hydrous minerals in country rocks results in an increase in the salinity of the residual fluids. To attain salinities close to twice that of seawater, as in fluids trapped by the inclusions in BH-10 and BH-149, approximately one half of the mass of seawater in
the evolving hydrothermal solution must be consumed by hydration reactions. Hydrous minerals are abundant in altered rocks in the stratigraphic footwall of the Rising Star and Bully Hill horizons. Loss-on-ignition gains, which largely represent additions of $\text{H}_2\text{O}$, in samples from this area range from 100 to 450% (see CHAPTER 7). Hydrous alteration mineral phases are also abundant regionally in the Bully Hill rhyolite and Dekkas andesite.

In a hypothesis of mixing at the site of deposition, seawater represents the low salinity endmember, and the unmixed hydrothermal endmember has a salinity in excess of 6 equivalent weight percent NaCl. Since the seawater endmember would presumably have a much lower temperature than the hydrothermal endmember, the lack of an increase in homogenization temperatures as salinity increases from zones 1 to 15a is not consistent with the mixing hypothesis. If mixing is an important process, either the temperature data are flawed or the seawater endmember was heated prior to mixing without experiencing a significant salinity increase.

The alternation of fluid inclusion-rich zones with relatively inclusion-poor zones in BH-10 and SH-41 quartz records episodic conditions in the growth of the crystals. The inclusion-rich zones were probably formed during periods of rapid, dendritic growth in the crystals (Roedder, 1984). This suggests that the hydrothermal solutions underwent episodic physicochemical changes which led to supersat-
uration and rapid precipitation of quartz. Decreases in temperature and/or pressure are the most efficient processes for quartz deposition; the solubility of quartz is nearly independent of pH, ionic strength and redox reactions (Holland and Malinin, 1979, and the references within). Episodic boiling or mixing with cold seawater (taking into account the effects of dilution upon mixing) are two possible mechanisms which could have led to quartz supersaturation in the crystals. If mixing with seawater caused quartz supersaturation, salinities of inclusions within the inclusion-rich zones should reflect the seawater component. The salinities of five inclusions from zone 6 of BH-10 quartz, the only data obtained from an inclusion-rich zone in the sample, do not deviate from the gradually increasing salinity trend of the sample as a whole. This suggests that mixing with cold seawater did not cause the formation of the inclusion-rich zones in this sample.

The limited salinity data from primary inclusions of SH-41 quartz are consistent with the results from BH-10 quartz and barite. The salinities of the pseudosecondary inclusions in SH-41 quartz range to much higher values, however. The wide range of salinity values within single pseudosecondary planes is particularly difficult to explain. Two mechanisms could explain the variation: leakage of fluids into the inclusions, or mixing of fluids during entrapment. In the first case, variable amounts of presum-
ably low salinity fluids leak into the inclusions and replace some of the primary fluids, which have salinity values close to 12 equivalent weight percent NaCl.

In the second mechanism, fractures in the quartz crystals fill with hydrothermal fluids which are actively mixing, the fluids precipitate quartz and inclusions are trapped as the fractures progressively heal. In this case, the inclusions are actually a special case of primary inclusions. The lower limit of salinity values again suggests that the mixed fluids have a low salinity seawater component and a high salinity hydrothermal component. Consideration of the spatial arrangement of inclusions within single pseudosecondary planes versus their salinity values shows the presence of two dimensional salinity gradients within some of the planes. Although the data are too limited to provide convincing evidence, these relationships are consistent with a mixing mechanism.

Regardless of the process, the salinity data from pseudosecondary inclusions in quartz and the primary inclusions in barite from SH-41 document the existence of relatively high salinity fluids. In fluid inclusion studies of Kuroko deposits, the highest salinities reported are about 8 equivalent weight percent NaCl (Urabe and Sato, 1978). There are no evaporites reported in the Nosoni, Dekkas, Bully Hill or older formations which could act as a source for high salinity fluids. In order for the wallrock
hydration mechanism proposed by Pisutha-Arnond and Ohmoto (1983) to account for salinities as high as 12 weight percent NaCl, 70% of the water in the initial seawater solution must be consumed. This seems unreasonably high. Unless an unknown source or mechanism provided a high salinity source, a magmatic component to the fluids which formed the stockwork mineralization represented by SH-41 is indicated.
CHAPTER 10

SULFUR ISOTOPES

Introduction

The sulfur isotopic compositions of 68 samples from the Bully Hill area are presented in Table 4. Analytical uncertainty is ± 0.2 per mil. Sample locations are presented on Figures 2 and 21.

The four $\delta^{34}S$ values of syngenetic sulfides from the Rising Star and Bully Hill mines are from composite sphalerite + galena separates. Stage 2a sphalerite makes up over 90 weight percent in each of the separates. The addition of such small amounts of galena to the sphalerite samples will not significantly alter the $\delta^{34}S$ values from those of pure sphalerite. For example, if the galena has a $\delta^{34}S$ value of +3 per mil, the addition of 10 weight per cent galena to the sphalerite alters the $\delta^{34}S$ value of pure sphalerite by less than 0.3 per mil.

The barites extracted from the matrices of the syngenetic sulfide ores are composite samples of several stages of mineralization. The samples are dominated by Stage 4 barite; the amount of barite from Stages 1 and 2a which is recrystallized or masked by the Stage 4 barite is difficult to determine.
Table 4. Sulfur Isotope Data

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RISING STAR HORIZON MINERALIZATION

BULLY HILL HORIZON MINERALIZATION

| BH0-1     | PY      | A     | 0.4                          |
| BH0-2     | BA      | S     | 22.5                         |
| McC       | PY      | C     | 1.5                          |
| BH-11     | BA-g    | A     | 19.3                         |
| BH-27     | PY      | A     | -0.6                         |
| BH-27     | BA-w    | A     | 15.0                         |
| BH-59     | PY      | B     | 0.1                          |
| BH-61     | PY      | B     | -0.7                         |
| BH-61     | BA-g    | B     | 21.8                         |
| BH-64     | PY      | C     | 1.2                          |
| BH-77     | BA-w    | B     | 13.3                         |
| BH-99     | BA-g    | A     | 22.7                         |
| BH-104    | PY      | A     | 0.5                          |
| BH-146    | BA-w    | A     | 14.2                         |
| BH-149    | BA-g    | A     | 21.6                         |
| BH-151-A  | BA-g    | A     | 22.1                         |
| BH-242    | PY      | A     | 0.4                          |
| BH-300    | SP+GN   | 2a    | -6.4                         |
| BH-500    | BA      | 4     | 14.1                         |
| BH-500    | SP+GN   | 2a    | -5.5                         |
| BH-600    | BA      | S     | 14.4                         |
| GE-16-1   | PY      | B     | 2.7                          |
| GE-16-2   | BA-w    | B     | 15.7                         |
| GE-49     | BA-w    | B     | 12.4                         |

COPPER CITY HORIZON

<p>| CCD-1     | BA      | S     | 15.2                         |
| CCD-2     | PY+SP   | 2b    | -0.6                         |</p>
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<th>Habit(^2)</th>
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**SHASTA MAY BLOSSOM MINERALIZATION**

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<td>SM-22-B</td>
<td>PY</td>
<td>R</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**NOSONI FORMATION**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineral(^1)</th>
<th>Habit(^2)</th>
<th>(\delta^{34}S) (per mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH-1</td>
<td>PY</td>
<td>D</td>
<td>-26.1</td>
</tr>
<tr>
<td>SH-32</td>
<td>PY</td>
<td>D</td>
<td>-2.4</td>
</tr>
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**DEKKAS ANDESITE**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineral(^1)</th>
<th>Habit(^2)</th>
<th>(\delta^{34}S) (per mil)</th>
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</thead>
<tbody>
<tr>
<td>BH-217</td>
<td>PY</td>
<td>K</td>
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<td>GE-46</td>
<td>PY</td>
<td>C</td>
<td>-0.5</td>
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<td>GE-58</td>
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<tr>
<td>HC-5</td>
<td>PY</td>
<td>D</td>
<td>-7.1</td>
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<tr>
<td>SH-38</td>
<td>PY</td>
<td>K</td>
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</table>

**BULLY HILL RHYOLITE**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineral(^1)</th>
<th>Habit(^2)</th>
<th>(\delta^{34}S) (per mil)</th>
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<td>SH-40</td>
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<td>PY</td>
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<tr>
<td>SH-1</td>
<td>PY</td>
<td>D</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)PY = pyrite; SP = sphalerite; GN = galena; BA = barite; AN = anhydrite; g = grey; w = white

\(^2\)1, 2a, 2b, 3a, 4 = mineralization Stages as outlined in text; A, B, C = mineralization in alteration Types 1, 2, and 3, respectively; D = disseminated pyrite; F = fine-grained pyrite; K = sulfide clast; M = frambooidal pyrite in mudstone; R = sulfide replacement; S = massive syngenetic barite
In this chapter, the isotopic results of the mineralization of the Bully Hill, Rising Star and Copper City mine areas are treated in detail. Included in this discussion are an evaluation of various mechanisms which might control the isotopic system, including inorganic, organic and seawater mixing processes; the seawater mixing model is examined numerically in detail. Conclusions are then drawn on the applicability of each of the mechanisms to the Bully Hill area system, and potential sources of the sulfur are evaluated. Finally, isotopic results from mineralization peripheral to the mine areas are evaluated.

Results

Barites have a $\delta^{34}\text{S}$ range of +12.4 to +24.1 per mil. Epigenetic grey (fetid) barites from Type 1 alteration zones from the three mine areas range from +15.5 to +24.1 per mil; 9 of the 12 samples have values greater than +21 per mil. One sample of grey barite from a sulfide-rich vein in Type 2 alteration stratigraphically above the Rising Star horizon has a $\delta^{34}\text{S}$ value of +21.8 per mil. Epigenetic white barites from Type 1 and 2 alteration zones related to the Bully Hill horizon, and one sample from the Bully Hill horizon less than a kilometer northeast of Bully Hill, range from +12.4 to +15.7 per mil. Massive syngenetic barites from the Bully Hill, Rising Star and Copper City mine areas range from +13.9 to +22.5 per mil; barites from the matrix of
syngenetic massive sulfide samples from the Bully Hill and Rising Star mines range from +12.4 to +19.6 per mil; and barite from the block within the lower Pit formation southwest of the Copper City mine has a $\delta^{34}S$ value of +12.6 per mil. One sample of anhydrite from the matrix of a massive sulfide sample from the Rising Star mine has a $\delta^{34}S$ value of +16.1 per mil.

Sulfide minerals have a $\delta^{34}S$ range of -26.1 to +50.4 per mil. Pyrites from concentrated disseminations and stockwork veinlets in Type 1 alteration zones from the three mine areas range from -0.6 to +2.6 per mil. Two samples of disseminated pyrite and one vein pyrite in Type 2 alteration stratigraphically above the Rising Star horizon have $\delta^{34}S$ values of +0.1, +2.7 and -0.7 per mil, respectively. Disseminated pyrite from Type 3 alteration zones lying stratigraphically between the Bully Hill and Rising Star horizons range from +0.1 to +1.5 per mil. A sample of disseminated pyrite from Type 3 alteration in the lower tuff unit of the Bully Hill-Rising Star mine area has a $\delta^{34}S$ value of -0.5 per mil. Pyrites from a fragment of massive pyrite within a lava flow near the top of the lava unit northeast of Bully Hill and from a sulfide clast within a silicified sedimentary(?) breccia at the base of the Bully Hill rhyolite at its westernmost occurrence in the Bully Hill area have $\delta^{34}S$ values of +29.4 and +50.4 per mil, respectively. Sphalerite + galena mixtures from syngenetic massive sulfide samples
from the Bully Hill and Rising Star mines range from -6.4 to -1.6 per mil, samples of sphalerite, pyrite and galena from massive sulfide ore of the Copper City mine area range from -0.6 to +3.0 per mil and pyrite from massive sulfide from the prospect on the Copper City horizon 1 kilometer west-southwest of Copper City has a $\delta^{34}S$ value of -15.8 per mil.

Two samples of disseminated pyrite from the Shasta May Blossom prospect have $\delta^{34}S$ values of -3.6 and +6.1 per mil. Pyrite from a semi-massive replacement pod in aphanitic andesite at the Shasta May Blossom has a $\delta^{34}S$ value of +5.0 per mil. Pyrite from the barite block in the lower Pit formation has a $\delta^{34}S$ value of -5.6 per mil. A thin layer of fine-grained pyrite from the calcitized tuff bed at the contact of the Bully Hill rhyolite and Pit formation exposed in Horse Creek has a $\delta^{34}S$ value of -14.3 per mil. Two samples of disseminated pyrite in Bully Hill rhyolite distant from highly altered and mineralized areas have $\delta^{34}S$ values of -7.1 and -2.4 per mil. Framboidal pyrite from a sample of Pit mudstone has a $\delta^{34}S$ value of -18.3 per mil.

Pyrite from a small prospect within the Nosoni formation near the Shasta Iron mine has a $\delta^{34}S$ value of -26.1 per mil. Disseminated pyrite in andesitic lava from the Dekkas andesite about 1.2 kilometers east of the Shasta Iron mine has a $\delta^{34}S$ value of -2.4 per mil.
Discussion

The ranges of $\delta^{34}S$ values from epigenetic and syngenetic barites and sulfides from the Bully Hill, Rising Star and Copper City mine areas are similar (Figure 48). This suggests that they were deposited from hydrothermal fluids which were similar in terms of their sulfur isotopic characteristics, and they will therefore be discussed together.

Bully Hill, Rising Star and Copper City Mine Areas

Sulfates. The coincidence of the ranges of epigenetic (grey together with white) and syngenetic barite $\delta^{34}S$ values strongly suggests that they are genetically related. Both have a lower limit of +12 per mil, which is within the range of Late Permian seawater sulfate (+11 ± 1 per mil; Holser et al., 1988). This strongly suggests that unmodified seawater was a source of sulfate to the barites, and that this seawater had a value of +12 per mil at the time of deposition of the Bully Hill rhyolite in the Bully Hill area. Epigenetic and syngenetic barite $\delta^{34}S$ values up to 12 per mil greater than the $\delta^{34}S$ value of contemporaneous seawater sulfate demand an additional source of sulfate as well.

In contrast to white epigenetic barites, grey epigenetic barites emit an odor of $H_2S$ gas when a crystal is freshly broken. The $H_2S$ gas is probably released from
Figure 48. Histogram of $\delta^{34}S$ values of sulfides and sulfates associated with mineralization from the Rising Star, Bully Hill and Copper City horizons. CC = Copper City; BH = Bully Hill; RS = Rising Star
ruptured fluid inclusions, which are abundant in grey barite crystals. This suggests that the grey barites precipitated from solutions which had low $\text{SO}_4^\text{2-}/\text{H}_2\text{S}$ ratios relative to the solutions which deposited the white barites. This geochemical distinction is accompanied by the isotopic differences of the grey and white barites.

**Sulfides.** Epigenetic pyrites from the three mine areas have $\delta^{34}\text{S}$ values of $+1 \pm 2$ per mil. This range overlaps the range of $0 \pm 3$ per mil suggested for magmatic sulfur (Ohmoto and Rye, 1979). The $+1$ per mil modal value is $11$ per mil lower than the seawater sulfate value indicated by the sulfate data; most Phanerozoic volcanogenic massive sulfide deposits have sulfides with $\delta^{34}\text{S}$ values about $17$ per mil lower than that of contemporaneous seawater (Sangster, 1976).

Syngenetic Stage 2b sphalerite and pyrite from the Copper City mine area have a range of $\delta^{34}\text{S}$ values which overlaps that of pyrite mineralization in the Type 1 alteration associated with the Copper City horizon. This suggests that the pyrites from the Type 1 alteration zone precipitated from solutions which ultimately formed the massive sulfide deposits.

Geochemical relationships in the massive sulfide mineralization from the Bully Hill area suggest that the $\text{SO}_4^\text{2-}/\text{H}_2\text{S}$ ratio of the hydrothermal solutions which precipitated the sulfide minerals may have decreased from Stage 2a
to Stage 3a mineralization (Figure 40). The $\delta^{34}S$ values increase from less than -1.5 per mil in Stage 2a sphalerite from the Bully Hill and Rising Star mines, to values between -1 and +1 per mil in Stage 2b sphalerite and pyrite from the Copper City mine area, to +3.0 per mil in the sample of Stage 3a galena from the Copper City mine area. The increasing $\delta^{34}S$ values are consistent with decreasing $SO_4^2-/H_2S$ ratios along the fluid evolution path shown on Figure 40.

The sphalerite composites extracted from specimens of syngenetic ore from the Bully Hill and Rising Star mines are samples of Stage 2a sphalerite. Since some Stage 2a sphalerite includes recrystallized Stage 1 sphalerite, an unknown isotopic signature inherited from Stage 1 may be included in the composite samples. The $\delta^{34}S$ values of these Stage 2a sphalerite samples are distinctly lower than those of epigenetic pyrites from underlying Type 1 alteration zones. This distinction remains when corrections are made for the differing fractionation factors of pyrite, sphalerite and galena with aqueous $H_2S$ (equations from Ohmoto and Rye, 1979).

Possible mechanisms to account for the shift to lower $\delta^{34}S$ values in the syngenetic Stage 2a sulfides include: (1) $H_2S$ in the hydrothermal fluid is partially oxidized close to the seawater/seafloor interface and becomes isotopically lighter; (2) the epigenetic sulfides precipitated from solutions which were isotopically distinct from
those that deposited the syngenetic sulfides, with the shift in isotopic values being the result of inorganically-con­trolled isotopic fractionation in the hydrothermal fluid; (3) $\text{H}_2\text{S}$ in the hydrothermal fluid mixes with a biogenic source of isotopically light $\text{H}_2\text{S}$ close to the seawater/sea­floor interface; and (4) the hydrothermal fluid mixes with cold seawater close to the seawater/seafloor interface, and the $\text{H}_2\text{S}$ becomes isotopically lighter through partial equili­bration with seawater sulfate.

The first possibility is unlikely since there is no plausible oxidant in large enough quantities available in the shallow subsurface (seawater sulfate will not oxidize $\text{H}_2\text{S}$). The remaining mechanisms will be examined below.

**Sulfide-sulfate relationships.** Assuming isotopic equilibrium and temperatures between 250 and 325°C, epigen­etic pyrite with $\delta^{34}\text{S}$ values of 1 ± 2 per mil would precip­itate from a hydrothermal fluid containing $\text{H}_2\text{S}$ with a $\delta^{34}\text{S}$ value of about 0 per mil (Figure 49). Aqueous $\text{SO}_4^{2-}$ in equilibrium with this $\text{H}_2\text{S}$, and barites which precipitate from the aqueous solution, would have $\delta^{34}\text{S}$ values of +19 to +24 per mil at these temperatures (equation 18, Ohmoto and Lasaga, 1982), which is the range of $\delta^{34}\text{S}$ values for grey barites. Since the temperature range is reasonable on the basis of the limited fluid inclusion data, this suggests that epigenetic pyrites and grey barites are isotopically linked. Textural evidence, however, suggests that the
Figure 49. Equilibrium isotopic relationships between aqueous sulfate and sulfide species at 250°C, where $\delta^{34}\text{S}_{\text{SS}} = 12$ per mil. Adapted from Ohmoto and Rye, 1979, figure 10.10.
epigenetic barite is later than the epigenetic pyrite. To satisfy both constraints, no significant fractionation of isotopic ratios in the hydrothermal fluids could have occurred during the interval of time between precipitation of the pyrites and barites.

There is a correlation of lower $\delta^{34}S$ values of Stage 2a sphalerite with lower $\delta^{34}S$ values of sulfate in the samples of massive syngenetic ores from the Rising Star and Bully Hill mines (samples BH-251, 252, 300 and 500; Table 4). The $\Delta$(barite-sulfide) values are grossly similar to those of the epigenetic mineralization, even though the barites are predominantly from Stage 4 mineralization. A genetic link in the sulfur isotopic systematics between the syngenetic sulfides and sulfates, and by inference the epigenetic and syngenetic sulfides and sulfates, is therefore indicated.

Isotopic temperatures. Attainment of isotopic equilibrium between mineral pairs is required for sulfur isotopic geothermometry. Textural evidence suggests that epigenetic and syngenetic barites and sulfides coexist but are largely not contemporaneous (CHAPTERS 3 and 8). In this case, attainment of isotopic equilibrium requires that no physicochemical or biogenic fractionation of isotopic ratios in the hydrothermal solution occurred in the interval of time separating precipitation of the mineral pairs, and that the minerals precipitated in isotopic equilibrium with the
solutions. If the temperature of the hydrothermal fluids decreased between deposition of the epigenetic sulfides and barites, meaningful isotopic temperatures can still be calculated as long as the aqueous sulfur species did not reequilibrate. In this case, the resultant disequilibrium isotopic ratios would preserve earlier high temperature relationships when isotopic equilibrium was attained.

Mineralization at the Rising Star mine is older than that of the Bully Hill mine, so that isotopic data from these mines can be used to evaluate the temporal constancy of isotopic ratios. The $\delta^{34}S$ ranges of epigenetic pyrite from the two areas are small and overlap. Epigenetic grey barites from the Rising Star mine have $\delta^{34}S$ values about 1 per mil higher than those from the Bully Hill mine, and the ranges from each mine area are again small. Clear modal values of epigenetic pyrite and grey barite emerge from the compilation of data from the Rising Star, Bully Hill and Copper City mine areas. On the basis of these limited data, the variation in isotopic ratios of epigenetic barites and pyrites between the time of mineralization of the Rising Star and Bully Hill mines is slight.

Table 5 presents isotopic temperatures indicated from sulfide-barite pairs from single hand specimens and modal values of data compiled from the three mine areas, using the equilibrium fractionation equation of Ohmoto and Lasaga (1982). If the criteria for isotopic equilibrium
Table 5. Sulfur Isotopic Temperatures

<table>
<thead>
<tr>
<th>Type of Isotopic Pair</th>
<th>Sample No.</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPIGENETIC GREY BARITE-PYRITE PAIRS</td>
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<td></td>
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<tr>
<td>Single handspecimen BH-61</td>
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<td>258</td>
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<tr>
<td>Rising Star horizon modes</td>
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<td>264</td>
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<td>Bully Hill horizon modes</td>
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<td>276</td>
</tr>
<tr>
<td>Copper City horizon modes</td>
<td></td>
<td>252</td>
</tr>
<tr>
<td>SYNGENETIC BARITE-PYRITE PAIRS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single handspecimen BH-251</td>
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<td>304</td>
</tr>
<tr>
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<td>259</td>
</tr>
<tr>
<td>Single handspecimen BH-300</td>
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<td>296</td>
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<tr>
<td>Single handspecimen BH-500</td>
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<td>338</td>
</tr>
<tr>
<td>Single handspecimen SH-40</td>
<td></td>
<td>316</td>
</tr>
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</table>

1Modes are derived from Figure 48
2Calculated using equation 18 of Ohmoto and Lasaga (1982), and correcting for (pyrite - H₂S) ≈ 1 in the temperature range of 200 to 400°C (Ohmoto and Rye, 1979).
outlined above were met, any of these pairs require legitimate consideration. Calculated temperatures range from 250 to 340°C. Epigenetic pairs, utilizing data from grey barites, yield temperatures ranging from 250 to 280°C, consistent with fluid inclusion results from associated quartz veins. Syngenetic mineral pairs yield temperatures ranging from 260 to 340°C. The higher temperature range in the syngenetic pairs is probably due to conditions imposed upon the isotopic system near the seawater-seafloor interface (see below).

Isotopic modeling. On the basis of the relationships outlined above, it is likely that the sulfate and sulfide mineralization formed from a hydrothermal system of uniform isotopic character. The isotopic data, therefore, provide constraints on geochemical models of the hydrothermal system. Such constraints include: the isotopic and physical distinction of grey and white epigenetic barites; the coincidence of the lower limit of epigenetic and syngenetic barite $\delta^{34}$S values with contemporaneous seawater sulfate; the 12 per mil range in sulfate values; and the anomalously low $\delta^{34}$S values in syngenetic Stage 2a sulfides at the Bully Hill and Rising Star mines.

Three mechanisms could have resulted in the observed isotopic ratios in the sulfide and sulfate mineralization: (1) inorganically-controlled equilibrium fractionation; (2) mixing of hydrothermal solutions with a biogenically-pro-
duced reservoir; and (3) mixing of hydrothermal solutions with seawater.

(1) Equilibrium fractionation: Physicochemical changes (e.g., temperature, pH and/or $f_{O_2}$) in the hydrothermal fluid cause isotopic fractionation which ultimately leads to variable $\delta^{34}S$ values in the barites and sulfides. The coincidence of limiting barite $\delta^{34}S$ values with the seawater value suggests that seawater sulfate was the principal source of sulfur in the hydrothermal fluid. Inorganically-controlled physicochemical variations imposed upon this fluid result in partial reduction of the seawater sulfate to $H_2S$ which, under equilibrium or near equilibrium conditions, results in isotopic fractionation between the aqueous sulfur species. In one widely accepted model, fractionation occurs as seawater sulfate is partially reduced at elevated temperatures by Fe++ contained in the volcanic rocks deep within the hydrothermal system (Sasaki and Kajiwara, 1971). This forms an evolved or modified seawater solution and results in shifts to higher $\delta^{34}S$ values of the remaining sulfate in the hydrothermal fluid. Reduced carbon contained within sediments of the Nosoni formation and Dekkas andesite could also act as the reducing agent.

The $\delta^{34}S$ values of aqueous $H_2S$ and $SO_4^{2-}$ are linked by fractionation factors, which vary as a function of temperature. Since temperatures consistent with other volcano-genic massive sulfide systems (e.g., Pisutha-Arnond and
Ohmoto, 1983) are indicated from the gross sulfide-sulfate relationships discussed above, and from isotopic mineral pairs, this model is consistent with the isotopic data.

The ranges of barite and sulfide $\delta^{34}S$ values record the isotopic shifts in the evolving seawater solution. Isotopically light Stage 4 barite, Stage 2a sphalerite and epigenetic white barite form from the least-evolved, relatively $H_2S$-poor solutions. More highly evolved, $H_2S$-rich solutions would deposit the epigenetic grey barites, stockwork pyrite mineralization, Stage 2b and 3a sulfides, and isotopically heavy Stage 4 barite.

The lower $\delta^{34}S$ values of the barites and sulfides either record the waxing stage of the hydrothermal system, when temperature is increasing and partial reduction of seawater sulfate ensues, or the waning stages of the system, when temperature decreases and/or reductants in the volcanic pile are consumed and partial reduction gradually ceases.

Textural evidence in combination with the isotopic data suggests the following sequence of mineralization. The onset of mineralization produces Stage 1 and then Stage 2a minerals, which precipitate from modified seawater solutions characterized by $SO_4^{2-}/H_2S$ ratios of about 3 (Figure 49; $SO_4^{2-}/H_2S$ values are derived from Ohmoto and Rye (1979), fig. 10.10a, assuming a constant temperature of 250°C and $\delta^{34}S_{ES} = 12$ per mil). As the temperature of the hydrothermal system increases, the $SO_4^{2-}/H_2S$ ratio of the fluid decreases to
approximately 1 and epigenetic pyrite, epigenetic grey barite, and syngenetic minerals of Stage 2b are precipitated. Stage 3a and 3b mineralization form from the most evolved solutions, which have \( \text{SO}_4^2-/\text{H}_2\text{S} \) ratios of about 0.3. The \( \text{SO}_4^2-/\text{H}_2\text{S} \) ratio gradually increases as the hydrothermal system wanes, and is recorded by the range of \( \delta^{34}\text{S} \) values of epigenetic white barite and Stage 4 syngenetic barite. Syngenetic and epigenetic white barite with \( \delta^{34}\text{S} \) values near 12 per mil require \( \text{SO}_4^2-/\text{H}_2\text{S} \) ratios of at least 50 (Figure 49).

The \( \text{SO}_4^2-/\text{H}_2\text{S} \) ratios derived above are within the limits of each stage of mineralization imposed by Figure 40. The inorganic fractionation model requires the path of fluid evolution on Figure 40 to be the product of deep-seated processes, not the result of intra-mound processes. This in turn requires that the Stage 2a sphalerites analyzed were not synchronous with the sulfides analyzed from Stages 2b and 3a.

At least two similar episodes of evolving physico-chemical conditions (i.e., changes in temperature or \( f_{\text{O}_2} \)) within the hydrothermal system must have occurred to explain the spread in the isotopic data from both the Rising Star and Bully Hill mines. Two thermal cycles are required, since reductants within footwall rocks could not have been consumed twice, and abundant Fe\(^{2+} \) is still present within the Dekkas andesite. Thermal pulses could have been related
to igneous processes, manifested by the extrusion of the lavas which constitute the lava unit of the Bully Hill rhyolite. The lava unit is composed of two lava subunits capped by autobreccias, and deposition of each subunit is succeeded by a mineralization event culminating in massive sulfide and barite formation. These igneous processes could affect the hydrothermal system indirectly, through temperature changes, or directly, by addition of magmatic components (although the model requires no significant input of magmatic sulfur).

(2) Mixing with biogenic sulfur: Biogenic reduction of seawater sulfate close to the seawater/seafloor interface in a system semi-closed to sulfate produces a reservoir of isotopically heavy sulfate and light sulfide. This reservoir is available to mix with the hydrothermal solution, characterized by 0 per mil aqueous $\text{H}_2\text{S}$ and essentially no aqueous sulfate. Various sulfate isotopic reservoirs could be formed, depending on the degree of reduction and extent of replenishment of seawater sulfate. The variably-shifted biogenic sulfate is then available to combine with $\text{Ba}^{++}$ from the hydrothermal fluid to produce the observed range of $\delta^{34}\text{S}$ values in barite. The proposed reservoir must persist out of contact with seawater, and would be necessarily small.

Alternatively, biogenic reduction of seawater and/or hydrothermal sulfate within the environment of the growing sulfide mound produces isotopically light $\text{H}_2\text{S}$ which becomes
fixed in Stage 1 sulfides. Stage 1 pyrite from an outlying occurrence of massive sulfide mineralization on the Copper City horizon provides evidence of this biogenic component (−15.8 per mil; see below). Recrystallization and/or dissolution and reprecipitation of the isotopically light Stage 1 \( \text{H}_2\text{S} \) by Stage 2a processes could result in anomalously low \( \delta^{34}\text{S} \) values in Stage 2a sphalerites. The presence of remnant Stage 1 textures and minerals within samples from which the Stage 2a sphalerites were extracted is consistent with this model. Processes of inorganic fractionation or seawater mixing must be coupled with this mechanism to produce the observed ranges in barite mineralization, however.

(3) Mixing with seawater: The range in barite \( \delta^{34}\text{S} \) values represents a mixing trend between sulfate from unmodified seawater (+12 per mil) and hydrothermal fluids (≥+23 per mil). White epigenetic and isotopically light syngentic barites form from mixtures dominated by seawater sulfate, while grey barites and isotopically heavy syngenetic barites form from mixtures dominated by hydrothermal sulfate. 0 per mil \( \text{H}_2\text{S} \) in the hydrothermal fluid, which precipitated the stockwork pyrites, partially reequilibrates with aqueous sulfate, representing a mixture from hydrothermal and seawater sources, to produce the isotopically light syngentic sulfides. This process of mixing and partial equilibration couples light \( \text{H}_2\text{S} \) and heavy \( \text{SO}_4^{2−} \). The
source of sulfur in the hydrothermal fluid is essentially unconstrained by this model.

There is abundant evidence for mixing of the hydrothermal solutions with seawater at the seafloor/seawater interface. Albers and Robertson (1961) reported massive anhydrite and gypsum replacements of the Bully Hill rhyolite in lower levels of the Rising Star and Bully Hill mines. Anhydrite also occurs as a fine-grained matrix mineral in some of the samples of massive sulfide from the Rising Star mine. Anhydrite has retrograde solubility, and heated seawater reaches anhydrite saturation at approximately 110°C along the vapor pressure curve (Glater and Schwartz, 1976). Since the hydrothermal solutions probably vented at temperatures ≥250°C, anhydrite precipitation is predicted by the mixing model. Anhydrite formation through mixing of hot hydrothermal solutions with seawater has been documented at high-temperature submarine hydrothermal vents on the East Pacific Rise (Spiess et al., 1980), and isotopic constraints suggest that mixing of seawater with hydrothermal solutions has led to voluminous anhydrite precipitation at the Fukazawa and Kosaka mines in the Kuroko district (Farrell and Holland, 1983). The single analysis of anhydrite from the Rising Star mine has a δ34S value which lies between the modal grey barite and seawater sulfate values. The presence of Mg-rich chlorite mixed with barite in the matrix of the syngeneric ore samples is further evidence of mixing, as
heated seawater precipitates magnesium almost instantaneously (Seyfried and Bischoff, 1977)

In a review of recent data compiled from active seafloor hydrothermal vents, Franklin (1986) developed a model for the formation of the massive sulfide accumulations in which mixing of hydrothermal fluids with seawater plays a vital role. A mat of anhydrite, precipitated from heated seawater, forms a continually-renewing protective cap to the growing sulfide mound. This cap traps much of the emergent hydrothermal fluid. Infiltrating seawater mixes with and cools the retarded hydrothermal fluids, leading to the precipitation of the sulfide minerals. Cooled, spent fluids escape from the mound and form white smokers, as further hot hydrothermal solutions are introduced at the base of the mound.

**Seawater mixing calculations.** The seawater mixing model is clearly consistent with the sulfate isotopic data, and is supported by geologic data. In order to evaluate the sulfide isotopic affects of mixing and reequilibration, the mixing process is modeled numerically here.

Variables used in the calculations include:

(1) Properties of the hydrothermal fluid: $\delta^{34}S_{SO_4} = +23$ per mil and $\delta^{34}S_{H_2S} = 0$ per mil; $\Sigma S = 10^{-4.5}$ m to $10^{-4}$ m; $SO_4^-/H_2S$ ratio = 0.1 to 1. The use of $\delta^{34}S$ values indicated by modal stockwork pyrite (with $\Delta_{(pyrite-H_2S)} = 1$) and grey barite ignores the possibility of any mixing prior to pre-
cipitation of the epigenetic mineralization. Hydrothermal fluids which precipitated Stage 2b minerals probably had \( \text{SO}_4^{2-}/\text{H}_2\text{S} \) ratios of between 0.1 and 1, and \( \Sigma S \) contents of between \( 10^{-4} \) and \( 10^{-4.5} \) m (Figure 40 and discussion in CHAPTER 8) before entering the environment of deposition of Stage 2a mineralization.

(2) Properties of seawater: \( \delta^{34}\text{S}_{\text{SO}_4} = \pm 12 \) per mil; \( \Sigma S = 0.03 \) m (assuming the composition of Permian seawater was approximately that of modern seawater).

(3) Properties of the mixed fluid: \( \Sigma S = 10^{-4} \) to \( 10^{-3} \) m; \( \text{SO}_4^{2-}/\text{H}_2\text{S} = 0.1 \) to 100; temperature = 250°C. Thermochemical data in combination with assumptions underlying the delineation of the Stage 2a field of mineralization on Figure 40 control the values of total aqueous sulfur and approximate \( \text{SO}_4^{2-}/\text{H}_2\text{S} \) ratio of the mixed fluids. The temperature of the mixture controls equilibrium fractionation of the aqueous sulfur species and the time necessary to obtain a specific degree of equilibration. The sulfur isotopic data suggest that the stockwork mineralization in Type 1 alteration zones formed at temperatures of 250 to 280°C, temperatures which are consistent with fluid inclusion data. A temperature of 250°C is valid in the calculations as long as the amount of seawater in the mixture is low.

(4) Isotopic values of sulfides precipitated from the mixed aqueous solution: -1.6, -3.8, -5.5 and -6.4, per mil
values of syngenetic Stage 2a sphalerite from the Bully Hill and Rising Star mines).

An isotopic balance equation, modified from Eastoe, Solomon and Garcia-Palomero (1986) to include aqueous hydrothermal sulfate, was used to calculate mixing ratio (w) and degree of attainment of equilibrium (F) for each of the four samples, where F is defined as

$$F = \frac{\Delta_f - \Delta_i}{\Delta_e - \Delta_i}$$  \hspace{1cm} (1)$$

where

$$\Delta = \delta^{34}S_{SO_4} - \delta^{34}S_{H_2S}$$

and subscripts i, f and e refer to initial, final and equilibrium states, respectively:

$$w \cdot (m_{SO_4,sw}) \cdot \delta_{sw} + (1-w) \cdot (m_{SO_4,ht}) \cdot (\delta_{SO_4,ht}) + (m_{H_2S,ht}) \cdot (\delta_{H_2S,ht}) = \delta_{SO_4,mix} \cdot ([w \cdot (m_{SO_4,sw}) + (1-w) \cdot (m_{SO_4,ht})] + (1-w) \cdot (m_{H_2S,ht}) \cdot (\delta_{H_2S,mix})$$  \hspace{1cm} (2)$$

where

$$\delta_{SO_4,mix} = \Delta_f + (\delta_{H_2S,mix})$$  \hspace{1cm} (3)$$

and, rearranging equation (1)

$$\Delta_f = F \cdot (\Delta_e - \Delta_i) + \Delta_i$$  \hspace{1cm} (4)$$
where

\[ \Delta_i = (\delta_{SO4,mix,i}) - (\delta_{H2S,ht}) \]  

(5)

where

\[ \delta_{SO4,mix,i} = \frac{w \cdot m_{SO4,sw} \cdot \delta_{SO4,sw} + (1-w) \cdot m_{SO4,ht} \cdot \delta_{SO4,ht}}{w \cdot m_{SO4,sw} + (1-w) \cdot m_{SO4,ht}} \]  

(6)

where \( m \) = molality, \( \delta = \delta^{34}S \), \( w = \frac{\text{weight}_{sw}}{\text{weight}_{(sw + ht)}} \)

and subscripts \( sw, ht \) and \( mix \) refer to seawater, hydrothermal fluid and mixture, respectively.

Figure 50 presents the results from the modeling of a hydrothermal solution with \( ES = 10^{-4} \) m and \( SO_4^2-/H_2S \) ratio = 1. The maximum mixing ratio, constrained by \( SO_4^2-/H_2S \leq 100 \) in the mixed fluid, is 0.14. The \( F = 1 \) curve is generated by solving equation (2) for \( \delta_{H2S,mix} \) at various mixing ratios. The horizontal line at the top of the graph is the \( F = 0 \) line. The value of \( F \) for any value of \( \delta_{H2S,mix} \) can be solved graphically, as \( F \) varies linearly along a vertical line drawn between \( F=0 \) and the \( F=1 \) curve at any specified mixing ratio. The dashed lines are contours of \( \delta_{SO4,mix} \) values within the field of possible values of \( \delta_{H2S,mix} \) generated by solving equation (3).

The low mixing ratios are deceiving, since much of the sulfate in seawater would be stripped by anhydrite
Figure 50. Graph showing the $\delta^{34}S$ values of aqueous sulfide and sulfate at various mixing ratios and degrees of attainment of equilibrium. Symbols are explained in text.
precipitation. The values of \( w \) therefore represent equivalents of seawater at a sulfate concentration of 0.03 m.

The Stage 2a sphalerite isotopic results can be produced by the processes of mixing and partial reequilibration of aqueous sulfur species. The time necessary to achieve the various degrees of equilibrium presents a constraint on the applicability of the model, however.

The time \( (t) \) required for various mixtures to attain the specified degree of equilibrium is a function of temperature, pH, F and total sulfur concentration of the mixed fluid, and can be solved using the rate of the sulfur isotopic exchange reaction in the pH range of 4 to 7 determined by Ohmoto and Lasaga (1982). Table 6 presents \( t \) for the modeled \( \delta^{34}S \) values at various mixing ratios. At the limiting mixing ratio of 0.14, times of 1 to 3.5 years are necessary to achieve the observed sulfide \( \delta^{34}S \) values. Values of coexisting sulfates are approximately 12 per mil at this mixing ratio. Mixing ratios successively less than 0.14 yield progressively greater values of \( t \), since lower \( \delta_{\text{H}_2\text{S},\text{mix}} \) values require significantly greater reequilibration times, and constrain coexisting sulfate to higher \( \delta^{34}S \) values.

An \( \text{SO}_4^{2-}/\text{H}_2\text{S} \) ratio of 0.1 in a hydrothermal fluid with \( \Sigma S = 10^{-4} \) m allows greater mixing ratios (maximum \( w = 0.23 \)) than those modeled above, and therefore lower \( \delta^{34}S \) values of coexisting sulfates are possible. The higher concentration of sulfur in the mixed fluids also decreases \( t \) values by
Table 6. Reequilibration Times For Various Mixture Ratios

For \( \Sigma S_{ht} = 10^{-4} \text{ m, } \frac{SO_4}{H_2S} = 1 \):

<table>
<thead>
<tr>
<th>Mixing ratio</th>
<th>-1.6</th>
<th>-3.8</th>
<th>-5.5</th>
<th>-6.4</th>
<th>( \delta H_2S_{mix} )</th>
<th>( R_{mix} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.001</td>
<td>111</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>(years) 2</td>
<td>2</td>
</tr>
<tr>
<td>.003</td>
<td>25</td>
<td>91</td>
<td>---</td>
<td>---</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>.005</td>
<td>19</td>
<td>55</td>
<td>258</td>
<td>---</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>.010</td>
<td>9</td>
<td>26</td>
<td>104</td>
<td>152</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>.015</td>
<td>6</td>
<td>17</td>
<td>28</td>
<td>35</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>.14</td>
<td>0.7</td>
<td>2</td>
<td>3</td>
<td>3.5</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

For \( \Sigma S_{ht} = 10^{-4} \text{ m, } \frac{SO_4}{H_2S} = 0.1 \):

<table>
<thead>
<tr>
<th>Mixing ratio</th>
<th>-1.6</th>
<th>-3.8</th>
<th>-5.5</th>
<th>-6.4</th>
<th>( \delta H_2S_{mix} )</th>
<th>( R_{mix} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.001</td>
<td>124</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>(years) 0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>.003</td>
<td>34</td>
<td>110</td>
<td>329</td>
<td>---</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>.005</td>
<td>19</td>
<td>57</td>
<td>108</td>
<td>164</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>.010</td>
<td>9</td>
<td>26</td>
<td>44</td>
<td>59</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>.015</td>
<td>6</td>
<td>17</td>
<td>28</td>
<td>36</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>.02</td>
<td>4</td>
<td>13</td>
<td>21</td>
<td>27</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>.03</td>
<td>3</td>
<td>8</td>
<td>14</td>
<td>17</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>.23</td>
<td>0.4</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

\( R = (\frac{SO_4}{H_2S})_{mix} \)
about one half at the limiting mixing ratio (Table 6). For hydrothermal solutions with $\Sigma S = 10^{-4.5}$ m, values of $t$ are slightly higher than those shown in Table 6 due to lower concentrations of sulfur in the mixed fluids.

Cathles (1983) estimated that the time required to form a typical Kuroko deposit was between 100 and 5,000 years on the basis of numerical modeling of the hydrothermal systems, with a single lens of massive sulfide probably forming in 500 years or less. Ohmoto et al. (1983), largely on the basis of sedimentation rates and thicknesses of sediments included within sulfide lenses in the Hokuroku district, estimated a time range between 200 and 50,000 years for the formation of a single massive sulfide lens.

Franklin (1986) considered that several tens or hundreds of years of venting of solutions at one site are necessary to form the larger ($\geq 10^6$ tonnes) accumulations of sulfides in modern black smoker environments.

If the model for growth of sulfide mounds in modern oceans proposed by Franklin (1986) is applicable to ancient land arc environments, the time limits modeled for the isotopic data are within the active life span of a mound. Hot hydrothermal solutions could potentially pond within the mound, and the ponded solutions could then mix with cooler seawater which infiltrates the mound. The temperature of the mixture could be buffered by the ambient temperature of
the mound, which is maintained by constant influx of hydro-
thermal fluids. High mixture temperatures could by main-
tained even when mixing ratios are high if this process 
operated. The benefits of higher mixture temperatures to 
the model are partially offset by the probable removal of 
much of the seawater sulfate in the mixture by precipitation 
of anhydrite, however. As the hydrothermal system col-
lapses, seawater mixing could descend into the footwall 
rocks and cause the formation of the paragenetically-late 
white and grey barites.

Although the resident times of ponded fluid in the 
growing sulfide mound might locally reach several tens or 
even hundreds of years in remote areas of the mound, modeled 
times much greater than the minimum values of t presented in 
Table 6 are probably unreasonable. The minimum t values 
impose tight limits on possible mixing ratios, $\delta^{34}S$ values 
of contemporaneous sulfate, and geochemical conditions of 
formation of Stage 2a sulfides (Figure 40). In addition, 
FeS contents demand $SO_4^2-/H_2S$ ratios $\leq 10$ in at least some of 
the Stage 2a sphalerites (Figure 40). In the absence of 
corroborative $\delta^{34}S$ values of coexisting Stage 2a barite, 
these limits suggest that mixing alone is not responsible 
for the observed isotopic data.

Conclusions on Isotopic Models. Inorganic frac-
tionation is the only mechanism which, on its own, is con-
sistent with all isotopic constraints. This does not ex-

clude the possibility that processes of seawater mixing or biogenic fractionation operated as well, however. Biogenic processes are interpreted to have produced fractionation of sulfur elsewhere in the Bully Hill area (see below). Mixing with seawater sulfate, with little or no isotopic reequilibration of aqueous sulfide species, is probably an important process in the formation of the white epigenetic barite and isotopically light syngenetic barite, where inorganic fractionation processes alone would need to produce $\text{SO}_4^-/\text{H}_2\text{S}$ ratios in excess of 50.

**Source of Sulfur.** The ultimate source of sulfur in the hydrothermal system(s) which formed the deposits at the Bully Hill, Rising Star and Copper City mine areas is constrained to be seawater if inorganic reduction of sulfate was the sole mechanism which produced the observed isotopic ratios. As discussed above, however, mixing of the evolved seawater solutions with unmodified seawater sulfate at the seawater-seafloor interface probably occurred. If this was the case, the lower limit of barite $\delta^{34}\text{S}$ values at the value of seawater sulfate does not limit possible sulfur sources to seawater alone.

The models proposed by Franklin (1986) and Eldridge et al. (1983) for the formation and growth of sulfide mounds on the seafloor suggest that the position of Stage 3 mineralization in the lower, central portion of the mound would serve to insulate it from physicochemical processes, such as
mixing with seawater, which operated within the mound environment. Solutions which precipitated Stage 3a and 3b mineralization would therefore most closely reflect the geochemistry of discharging hydrothermal fluids.

The sample of Stage 3a galena has the highest $\delta^{34}\text{S}$ value of any sulfide from the Bully Hill, Rising Star and Copper City mine areas. Under equilibrium conditions at 250°C, this galena would precipitate from aqueous $\text{H}_2\text{S}$ with a $\delta^{34}\text{S}$ value of approximately +5 per mil. Figure 40 suggests that Stage 3a mineralization precipitated from solutions characterized by $\text{SO}_4^-/\text{H}_2\text{S}$ ratios of 0.1 to 1. If these conditions reflect those of the fluids within the hydrothermal system, and the hydrothermal system was closed to sulfide (i.e., no major loss of aqueous $\text{H}_2\text{S}$ through precipitation of sulfide minerals prior to galena precipitation), the $\delta^{34}\text{S}$ value of the galena can be used to indicate the $\delta^{34}\text{S}$ value of total sulfur in the hydrothermal system.

Under equilibrium conditions at a temperature of 250°C, aqueous $\text{SO}_4^-/\text{H}_2\text{S} = 0.1$ to 1.0 and $\delta^{34}\text{S}$ value of hydrothermal $\text{H}_2\text{S} = +5$, the $\delta^{34}\text{S}$ value of total sulfur in the hydrothermal solution lies between 7 and 17 per mil (Ohmoto and Rye, 1979, equation 10.9). These calculations require that coexisting aqueous sulfate had a $\delta^{34}\text{S}$ value of 29 per mil (since $\Delta = 24$ per mil at 250°C); no barites record isotopic ratios this high. At 300°C, coexisting sulfate has a $\delta^{34}\text{S}$
value of 25 per mil, for the same range of total sulfur $\delta^{34}$S values.

Stage 2b mineralization also developed in lower portions of the sulfide mound. Using the same geochemical constraints outlined above, Stage 2b pyrite and sphalerite, which have $\delta^{34}$S values identical to epigenetic pyrite, yield a range of total sulfur $\delta^{34}$S values of 2 to 12 per mil and a coexisting sulfate $\delta^{34}$S value of 24 per mil at 250°C.

Seawater sulfate ($\delta^{34}$S = 12 per mil) is within the calculated range of total sulfur $\delta^{34}$S values. Ohmoto and Rye (1979) calculated that fluids expelled from felsic magmas, given the proper geochemical conditions, could have $\delta^{34}$S values of aqueous H$_2$S which evolve to as high as 7 per mil. The isotopic values of igneous sulfur in the Dekkas andesite and Bully Hill rhyolite are not constrained by data from this study, but are probably within the range of magmatic fluids. The source of sulfur therefore cannot be rigorously constrained by the sulfur isotopic data.

Urabe (1987) considered that the overlap of the sulfur isotopic values of Kuroko ore sulfides ($+5 \pm 4$ per mil) with values of igneous sulfur reflects a magmatic source of sulfur. Seawater sulfate cannot be excluded as the sulfur source, however, since inorganic reduction of contemporaneous seawater sulfate ($+20$ per mil) can account for the isotopic compositions of the Kuroko sulfides. In the case of the Bully Hill ores, Late Permian seawater
sulfate had a $\delta^{34}S$ value of +12 per mil, the lowest value in the history of the Earth. By analogy with the Kuroko isotopic system, therefore, Bully Hill ore sulfides should have negative $\delta^{34}S$ values. Stage 2b syngenetic sulfides, 3a syngenetic sulfides, and epigenetic pyrites in the Bully Hill ore systems, which apparently did not incorporate significant biogenic or unmodified seawater components, have a strong modal $\delta^{34}S$ value of +1 per mil. This may give evidence of a magmatic source of sulfur at Bully Hill.

**Other Mineralization**

Framboidal pyrite from a sample of Pit Formation mudstone remote from massive sulfide mineralization has a $\delta^{34}S$ value of -18 per mil, which is significantly lower than $\delta^{34}S$ values of any of the sulfides associated with the three mine areas. This isotopically light sulfide was probably produced diagenetically by bacteriogenic reduction of seawater sulfate in a euxinic environment. Pyrite from the calcitized tuff in Horse Creek and Stage 1 colloform pyrite from the massive sulfide prospect west-southwest of Copper City have $\delta^{34}S$ values of -14 and -16 per mil, respectively. It is likely that the sulfur in these pyrites also has a predominantly biogenic origin.

The two samples of pyrite from fragments within rocks of the Bully Hill rhyolite have $\delta^{34}S$ values of +29 and +50 per mil. The pyrite in these fragments is interpreted
to have been produced biogenically by the low temperature reduction of seawater sulfate in a system closed to $\text{SO}_4^{\text{2-}}$ and open to $\text{H}_2\text{S}$, and were subsequently incorporated into their host rocks as exotic clasts.

The massive barite block from the lower Pit formation has pyrite with a $\delta^{34}\text{S}$ value of $-6$ per mil and barite with a value of $+12$ per mil. These values coincide with the ranges of syngenetic mineralization at the Bully Hill and Rising Star mines, and are likely to be of similar origin.

The three samples of epigenetic pyrite ($\delta^{34}\text{S} = -3.6$, $+5.0$ and $+6.1$ per mil) from the Shasta May Blossom area fall outside the range of $\delta^{34}\text{S}$ values of epigenetic pyrite from the Rising Star, Bully Hill and Copper City mine areas. The sample with the lowest $\delta^{34}\text{S}$ value may have formed by any one of the three mechanisms considered in the evaluation of the Bully Hill and Rising Star mineralization. The two pyrite samples with high $\delta^{34}\text{S}$ values may have precipitated from relatively evolved solutions with low $\text{SO}_4^{\text{2-}}/\text{H}_2\text{S}$ ratios, similar to Stage 3a galena from the Copper City mine. Alternatively, the sulfur in the pyrites had a source which is isotopically distinct from that of the main mine areas.

The two samples of disseminated pyrite ($\delta^{34}\text{S} = -7.1$ and $-2.4$ per mil) in the Bully Hill rhyolite northwest of Bully Hill and the sample of pyrite ($\delta^{34}\text{S} = -2.4$ per mil) from the Dekkas andesite east of the Shasta Iron mine occur within restricted zones of alteration and disseminated
mineralization. Their occurrence in rocks exhibiting anomalous degrees of alteration and mineralization with respect to surrounding rocks suggests that the pyrites are hydrothermal in origin, and therefore they do not represent $\delta^{34}S$ values of pristine igneous sulfur.

The single pyrite analysis from the Nosoni formation ($\delta^{34}S = -26.1$ per mil) is from a dump to a small prospect near the Shasta Iron mine, and may be related to the hydrothermal system associated with the magnetite mineralization which occurs at the mine.
CHAPTER 11

DISCUSSION

Evolution of the Hydrothermal System

Regional Hydrothermal Alteration

There are few, if any, pristine volcanic rocks in the Bully Hill area. A district-wide hydrothermal event has altered volcanic rocks of the Bully Hill rhyolite and Dekkas andesite to quartz keratophyres and keratophyres. The process of keratophyrization involves the enrichment of sodium and quantitative depletion of potassium in the volcanic rocks.

Thermodynamic data suggest that alteration of felsic rocks by hydrothermal solutions with Na/K molar ratios of approximately 28 (equivalent to present-day unmodified seawater) at high water/rock ratios favors albite over potassium feldspar at temperatures $\geq 150^\circ$C, while potassium feldspar is favored at lower temperatures (Munha et al., 1980). These results are supported by experimental seawater-basalt reactions (e.g., Mottl et al., 1974). It is therefore likely that seawater-dominated solutions reacted with the volcanic rocks in the Bully Hill area at a temperature of 150°C or higher, resulting in the enrichment of Na and depletion of K in the rocks. This low temperature
alteration is interpreted to be the result of district-wide elevated temperatures within the volcanic pile at the time of deposition of the Dekkas andesite and Bully Hill rhyolite.

**Ore-forming Hydrothermal System**

**Source of Heat.** The orebodies of the Bully Hill and Rising Star mines formed within vent-proximal quartz-phyric felsic volcanic rocks which extruded from the cumulo dome northeast of Bully Hill. Both periods of mineralization occurred immediately following extrusion of autobrecciated lava from the vent. Copper City mineralization immediately overlies autobrecciated quartz phenocryst-poor dacitic lava. Flow-banded dacitic lavas with autobrecciated tops make up the bulk of the olistostromal portion of the Bully Hill rhyolite in the Copper City area. It is likely that these dacitic lavas vented near the Copper City mine. The source of energy for the hydrothermal systems which ultimately formed the Bully Hill-Rising Star and Copper City mineralization is interpreted to be the subvolcanic bodies of magma which fed the two vents. These intrusions would have served to provide local thermal anomalies within the regional elevated temperature regime in the volcanic pile. Neither of these hypothesized intrusions is presently exposed.

**Source of Hydrothermal Fluids.** Salinities of fluids which formed the Type 1 alteration zones are equal to or
greater than the salinity of average modern seawater. The coincidence of the lower limit of salinity of the hydrothermal fluid with seawater salinity suggests that seawater was a component of the hydrothermal fluid. The consistent, gradual increase in salinities at constant temperature of fluids which formed BH-10 quartz suggests that mixing of relatively hot high salinity hydrothermal fluids with unmodified seawater at the site of deposition did not occur, at least during deposition of the quartz. The high \( \delta^{34}S \) values of stockwork grey barite mineralization in the Type 1 zones suggest that little, if any, unmodified seawater sulfate mixed with the hydrothermal fluids at the site of deposition. The seawater component of fluids which formed Type 1 zones probably originated as pore water within the volcanic pile. If a circulation cell developed, additional seawater could have been added to the system by influxing at recharge sites.

Salinities almost twice that of seawater in fluids which precipitated BH-10 quartz were the result of deep-seated processes. Possible processes include high temperature evolution of the seawater solution through wallrock hydration reactions and/or mixing of the seawater with magmatic fluids.

The trend of gradually increasing salinities of fluids recorded in BH-10 quartz is punctuated twice by relatively high salinity events associated with development
of pseudosecondary planes of fluid inclusions (Figure 44). One of these events involved a fluid with a salinity of about 6 equivalent weight per cent NaCl, the highest in the sample. Pseudosecondary inclusions from SH-41 quartz contain fluids with salinities up to 3.5 times greater than that of seawater, suggestive of a magmatic component. The coupling of these anomalously high salinities with intragrowth cracking of quartz crystals within Type 1 zones suggests that tectonic events may have been associated with periodic magmatic inputs to the modified seawater solutions.

**Alteration of Footwall Rocks.** Alteration Types 1, 2 and 3 occur in a zone stratigraphically below the productive portions of the Bully Hill and Rising Star horizons. This zone probably represents the upper portion of 'pipes' of extreme hydrothermal alteration typical of most hydrothermal vent-proximal massive sulfide systems (Franklin et al., 1981). In the Bully Hill-Rising Star mine area, alteration Types 1 and 2 occur as two extensive silicified caps, one at each mine, above Type 3 alteration zones. The structurally-restored composite zone of extreme hydrothermal alteration in the Bully Hill-Rising Star mine area covers approximately one cubic kilometer; the alteration zone in the Copper City area is significantly smaller, although it is largely unexposed owing to structural effects.

Rocks within the top of the alteration pipe in the Bully Hill-Rising Star mine area are characterized by per-
vasive depletion of CaO and Na₂O, and addition of K₂O and especially SiO₂. Similar geochemical trends for the alkalies and calcium are typical of alteration pipes in most massive sulfide districts (e.g., Franklin et al., 1981, and references within); quartz is a significant product of alteration in Kuroko ore systems (Date et al., 1983; and Urabe et al., 1983).

Quartz and sericite are the predominant alteration minerals in the alteration zones associated with the Bully Hill-Rising Star ore system. Albite that formed during the regional low temperature alteration event reacted with acidic, potassium-bearing hydrothermal fluids:

\[ 3NaAlSi_3O_8 + 2H^+ + K^+ = KAl_3Si_2O_10(OH)_2 + 6SiO_2 + 3Na^+ \]

(resulting in additions of potassium and scavenging of sodium in the rocks, and the replacement of albite with quartz and sericite. Calcium-bearing phases were similarly replaced, and calcium was leached from the rocks. Potassium may have been supplied to the solutions by the albitization of K-feldspar in areas distant from the pipe at lower temperatures.

Significant quantities of silica were added to the rocks within the top of the pipe. The ubiquitous presence of quartz in footwall alteration assemblages suggests that hydrothermal fluids were saturated with silica. Precipitation of quartz probably resulted from conductive cooling
of hydrothermal fluids within the alteration pipe. Silica dumping was most extreme close to the seawater-seafloor interface in Type 1 and 2 alteration zones.

The cap of silicification represented by Type 1 and 2 zones developed over relatively long strike lengths relative to massive sulfide-sulfate mineralization; the exposed strike length of these zones along the Rising Star horizon is approximately five times longer than the known productive portion of the horizon. Type 1 and 2 zones are interpreted to have formed by unfocused venting of hydrothermal solutions. Quartz deposition, which initially may have been caused by mixing with seawater, resulted in sealing of the hydrothermal system. Episodic cracking of the seal by overpressuring of the hydrothermal system and/or tectonic processes could have led to sudden decrease in pressure and subsequent quartz supersaturation and precipitation. Breaking of the silicified seal served to localize venting of hydrothermal fluids, and repeated episodes of sealing, cracking and quartz dumping in these areas led to the formation of spatially restricted Type 1 zones. Dendritic growth in quartz crystals from Type 1 zones, producing fluid inclusion-rich zones, may record these episodic events.

The repeated sealing of the hydrothermal system led to lateral movement of fluids below the silicified cap. Fluid movement towards the paleobasin south of the cumulo dome resulted in the laterally-extensive Type 3 alteration
zone which presently underlies the west and southwest flanks of Bully Hill.

Once sufficiently developed, the silicified cap served to seal rocks within the pipe from seawater. This is reflected in the lack of chlorite as a common alteration phase in alteration Types 1, 2 and 3. Chlorite that might have formed early in the development of the alteration zones was subsequently replaced by quartz and sericite. Chlorite is a locally important alteration phase in rocks characterized by alteration Types 4 and 5, which formed in the shallow subsurface of the Bully Hill and Rising Star horizons, respectively, laterally beyond the impermeable silicified cap where seawater was able to infiltrate.

Formation of Syngenetic Mineralization. When venting of the hydrothermal fluids was restricted to a few discharge sites and was sustained for 100 years or more, significant sulfide-sulfate mineralization in the form of a mound could develop on the seafloor above the Type 1 alteration zones.

At temperatures ≥200°C, discharging fluids with salinities up to 12 weight per cent NaCl would have densities less than 1.0 g/cm³, and would therefore rise buoyantly in the open ocean (Solomon and Walshe, 1979). If cooling of these buoyant solutions was accomplished through mixing with cold seawater, the density of the mixture never exceed the density of seawater (Sato, 1972). Particulate
sulfides and sulfate minerals which formed in the rising plume settled to form bedded Stage 1 ore. Bacterial activity may have been widespread on the seafloor adjacent to vents, producing colloform and framboidal pyrite with low $\delta^{34}S$ values ($<-12$ per mil) which became incorporated in the Stage 1 ore. Replacement and recrystallization processes of Stage 2 and 3 ore formation ensued when Stage 1 ore blanket-ed the vents.

Geochemical changes in the hydrothermal fluids -- including decreases in both $\Sigma SO_4^{2-}$ and $H_2S$ contents, increase in $\delta^{34}S$ values of aqueous $H_2S$, and probable decrease in $SO_4^{2-}/H_2S$ ratio -- accompanied the change from deposition of Stage 2a to Stage 3a mineralization within the mound. These changes were controlled by both deep-seated processes within the hydrothermal system and intra-mound processes. Deep-seated processes which may have operated include wallrock interactions, inorganic isotopic fractionation and varying contributions of magmatic components. Intramound processes include mixing with unmodified seawater, which clearly could have influenced sulfate isotopic ratios, and incorporation of $H_2S$ and $SO_4^{2-}$ from minerals within the mound dissolved by later fluids. The relative importance of each of these processes can only be determined by further detailed isotopic analysis.

**Waning Stages of Mineralization.** Stage 4 and epi-genetic barite formed as temperatures in the hydrothermal
systems decreased. Decreasing temperatures led to increasing densities of the hydrothermal solutions, which resulted in reduced fluid flow and collapse of the system. Stage 4 mineralization retreated from the syngenetic mounds to the underlying Type 1 zones, and epigenetic grey barite was precipitated. Seawater encroachment into footwall rocks, largely restricted to Type 2 zones, resulted in fluid mixing and deposition of white epigenetic barite.

**Hydrothermal Cycles.** Both the Rising Star and Bully Hill ore systems proceeded independently to full maturity, i.e., relatively low temperature barite mineralization (Stage 4 and epigenetic barite) followed sulfide-rich mineralization (Stages 1, 2 and 3) at each mine, indicating the existence of two full thermal cycles. These cycles were probably controlled by magmatic activity in the subvolcanic environment of the cumulo dome, and are linked to extrusion of autobrecciated lavas of the lava unit.

**Source of Silica.** Rocks in the footwall of the Bully Hill-Copper City horizon have undergone voluminous introduction of silica by hydrothermal fluids. Possible sources of the silica include footwall rocks, seawater and fluids expelled from magma. Footwall rocks do not appear to be a viable silica source since none of the samples of the Bully Hill rhyolite and Dekkas andesite analyzed have low SiO₂ concentrations relative to unaltered equivalents (other more numerous and spatially extensive analyses of the Dekkas
andesite from the Bully Hill and adjacent areas also show no loss of SiO$_2$; C. J. Eastoe, 1989, personal communication). The silica content of seawater is about 1 to 10 ppm (Holland, 1978), necessitating huge volumes of seawater and an efficient precipitation mechanism to account for the silica gains. The solubility of quartz in hydrothermal fluids at temperatures between 150 and 350°C is 100 to 1500 ppm (Rimstidt and Barnes, 1980), or over 1 order of magnitude greater than the silica content of seawater, so that heated seawater would actually be undersaturated in quartz. Since footwall rocks cannot be invoked as a silica reservoir, hydrothermal fluids must have been saturated with quartz at their origin. Fluids expelled from high-level, evolved felsic magmas could meet this constraint.

**Comparison with Kuroko Ore Systems**

The geological characteristics of the late Permian Bully Hill area ore systems, including the geologic setting, mineralization, alteration of host rocks and fluid geochemistry, are remarkably similar to those of the Miocene Kuroko ore systems of Japan. The ores at Bully Hill can clearly be classified as kuroko-type mineralization. The geology of the Japanese Kuroko deposits, as typified by the well studied Hokuroku district, is compared with the Bully Hill area below.
The geologic environment of the Hokuroku district is quite similar to that at Bully Hill. The Kuroko deposits are hosted by an island arc volcanic succession which consists of andesitic to basaltic lavas and tuff breccias overlain by felsic lavas and tuffs which host the ore deposits. These rocks are overlain by mudstones, felsic tuffs and basaltic lavas (Tanimura et al., 1983). The felsic volcanics are made up of a lower lava-rich portion and an upper unit of lithic-rich tuff breccias and, locally, lava domes. The domes are typically 200 to 500 meters in diameter, commonly are autobrecciated and are commonly closely associated with massive sulfide mineralization, which occurs at the top of the upper unit. A significant difference between the two areas is the estimated depth of seawater at the time of ore deposition; Kuroko deposits are inferred to have formed at depths ≥2000 meters (Guber and Merrill, 1983), while the depth of seawater is interpreted to be significantly less at Bully Hill.

The mineralogy and distribution of both ore types and alteration assemblages in the two districts are also very similar. In a comparison of Japanese Kuroko deposits with Canadian examples, Urabe et al. (1983) described the mineralogic zoning at the Uwamuki deposits as follows: a core of quartz + sericite, a zone of sericite + chlorite + quartz which rims the core, and more distal alteration assemblages consisting of variable quantities of the same
minerals in addition to albite and kaolinite. As reviewed in CHAPTER 8, the mineralogy, texture and relative quantities of metals in the syngenetic and epigenetic mineralization of the Kuroko and Bully Hill ores are also quite similar.

The temperatures, salinities and sulfur isotopic compositions of Bully Hill hydrothermal fluids are generally similar to Kuroko ore fluids, although they differ somewhat in detail. Kuroko ore sulfides and sulfates have a $\delta^{34}S$ values ranging from 10 to 20 per mil less and 0 to 5 per mil greater, respectively, than 20 per mil contemporaneous seawater sulfate (Urabe, 1987). At Bully Hill, the range of ore sulfide $\delta^{34}S$ values relative to late Permian seawater sulfate (12 per mil) is identical to that of Kuroko, while sulfate values range up to 12 per mil greater than the seawater value. Temperatures and salinities from fluid inclusions from both areas are similar, although higher temperatures are recorded in some of the Kuroko inclusions (Pisutha-Arnond and Ohmoto, 1983) and some Bully Hill inclusions have salinities higher than those reported for Kuroko.
CONCLUSIONS

Important conclusions derived from this study are summarized below:

1. The Dekkas andesite is pervasively hydrothermally altered in the Bully Hill area. The secondary mineral assemblage in the andesitic lavas and pyroclastic deposits consists of chlorite, albite, iron oxides, calcite, epidote, pumpellyite, sphene, leucoxene, pyrite, quartz, sericite, prehnite and barite.

2. The Bully Hill rhyolite is made up of quartz phenocryst-poor dacitic lavas, which occur predominantly at the base of the formation, quartz-phyric rhyodacitic to rhyolitic lavas and lithic-rich tuff breccias, which form the bulk of the formation, and andesitic to basaltic volcanic deposits (upper mafic unit), which lie at the top of the formation.

3. The upper portion of the Bully Hill rhyolite and lowermost Pit formation are commonly lithologically complex and disrupted, and appear to have been deposited as large scale debris flows. The isolated bodies of mafic volcanic rocks which make up the upper mafic unit of the Bully Hill rhyolite may be blocks within the olistostromal megabreccia.
4. In the Bully Hill-Rising Star mine area the Bully Hill formation is divided into, from stratigraphic bottom to top, the lower tuff unit, lava unit, tuff breccia unit and upper tuff unit. These units were deposited subaqueously. The lava unit consists predominantly of massive rhyodacitic to rhyolitic flow-banded lavas. Two lava flow subunits are recognized, each capped with autobrecciated flows. The lower tuff and tuff breccia units are dominated by lithic-rich tuff breccias, deposited as submarine talus breccias. The upper tuff unit is lithologically heterogeneous, and may have formed in part as talus breccias and in part as debris flows.

5. The structure in the Bully Hill-Rising Star mine area is dominated by a tight south-plunging anticline partially overturned to the east, with a steeply west-dipping axial surface. This fold is younger than the regional relatively open northwest-trending fold set. The fold formed because of the strong rheological contrast between highly silicified rocks in the footwall of the Bully Hill mine orebodies and clay-rich lithologies in the hangingwall. A distinctive spaced cleavage is associated with this fold in homogeneous sericite-bearing rocks.

6. Seven alteration facies (Types 1 through 7) are defined in the Bully Hill area; Types 1 through 6 occur in the Bully Hill-Rising Star mine area. Type 1 alteration has
also been delineated in the Copper City mine area. Type 7 alteration occurs regionally.

Types 1, 2 and 3 form a zone of extreme hydrothermal alteration stratigraphically below the massive syngenetic mineralization. Type 1 alteration occurs irregularly along semi-conformable zones along and immediately below productive portions of massive sulfide horizons. Type 1 alteration consists of almost complete replacement of the protolith, commonly autobrecciated lava, by quartz. Type 1 zones are characterized by the presence of stockwork veinlets of quartz, barite and pyrite. Type 2 alteration is also associated with the immediate stratigraphic footwall of ore horizons, but is more extensive than, and partially encloses, Type 1 zones. Type 2 alteration is similar to Type 1, except that sericite is more abundant, silicification is less intense and stockwork mineralization is less well developed. Type 3 alteration forms an extensive zone of quartz + sericite ± calcite ± chlorite below the semi-conformable silicified cap formed by Types 1 and 2. Silicification is less intense and sericitization is more prevalent in this facies than in Types 1 and 2.

 Alteration Types 4 and 5 contain quartz, sericite, calcite and chlorite in varying amounts, and occur marginal to the alteration pipe. Type 6 alteration occurs in the immediate hangingwall the Bully Hill horizon, and differs from Types 1 through 5 by the lack of significant silicif-
ication and abundance of clay minerals. The Type 7 alteration assemblage occurs regionally in the Bully Hill rhyolite, and consists of quartz, albite, chlorite, epidote-clinozoisite, pyrite, sericite and leucoxene with or without kaolinite, calcite and iron-rich carbonate.

7. The alteration zone in the Bully Hill-Rising Star mine area formed by the interaction of ascending hydrothermal fluids with wallrocks below the seafloor. Cooling of the silica saturated solutions led to the development of an extensive silicified cap in the immediate subsurface which sealed the hydrothermal system and resulted in the formation of Type 2 zones. Repeated cracking and resealing of the silicified cap focused venting of the fluids and led to the formation of Type 1 zones. When the system was sealed, lateral fluid movement led to the development of Type 3 alteration.

8. The massive sulfide-sulfate ore bodies of the Rising Star and Bully Hill mines are located at the top of the lower and upper subunits, respectively, of the lava unit of the Bully Hill rhyolite.

10. The geology of the Copper City mine area is similar to that of the Bully Hill-Rising Star mine area. The Bully Hill rhyolite is composed of dacitic quartz phenocryst-poor lavas and tuffaceous deposits which are deformed into a north-trending anticline. Type 1 alteration and mineralization is developed at the upper contact of the
Bully Hill rhyolite, and immediately underlies the massive sulfide-sulfate mineralization of the Copper City horizon.

10. Mineralization in the vicinity of the Shasta May Blossom prospect occurs along the contact of highly silicified aphanitic andesitic lava of the upper mafic unit of the Bully Hill rhyolite and fine-grained sediments and reworked lithic-rich tuffs of the lower Pit formation. The contact is marked by an intensely silicified breccia containing fragments of fine-grained sediments and volcanic(?) rocks. Mineralization is made up of sulfide, carbonate and sulfate replacements of the volcanic rocks.

11. The volcanic rocks of the Bully Hill rhyolite in the Bully Hill-Rising Star mine area extruded from a vent approximately 1 kilometer northeast of Bully Hill at the site of a cumulo dome defined by Albers and Robertson (1961).

12. The mineralization of the Bully Hill area formed in a submarine volcanogenic environment. The lenses of massive sulfide-sulfate ore represent syngenetic accumulations on or immediately below the seafloor.

13. The Bully Hill and Copper City ore horizons may be coeval, and are younger than the Rising Star ore horizon. The potential for discovery of additional sulfide-rich syngenetic mineralization along these horizons is excellent.

14. Alkali contents of volcanic rocks of the Dekkas andesite, Bully Hill rhyolite and Pit formation define two
types of hydrothermal alteration: regionally-distributed keratophyrization and ore-proximal alteration.

15. Zr and TiO$_2$ remained immobile during the hydrothermal alteration reactions associated with ore-forming systems at the Bully Hill and Rising Star mines, and allow meaningful chemical classification of the volcanic rocks. Al$_2$O$_3$ also behaved isochemically in all but the most intensely altered samples. Nb and Y were somewhat mobile in many of the highly altered samples examined.

16. Keratophyrization resulted in the almost complete loss of K$_2$O and approximately 50% gain in Na$_2$O.

17. Alteration within the ore-proximal alteration is characterized by SiO$_2$ additions of up to 250%, K$_2$O additions of up to 60%, and almost total removal of Na and Ca. Significant leaching of Fe$_2$O$_3$ is also evident in all samples which are not heavily mineralized with pyrite. MgO was added in increasing amounts with increasing distance from ore horizons. Volume gains range from about 10% in Type 3 zones to 100 to 200% in Type 1 zones.

18. Significant quantities of SiO$_2$ have been added to the Dekkas andesite, and it is therefore not a tenable source of silica to the hydrothermal fluids.

19. Massive syngenetic sulfide-sulfate mineralization consists of sphalerite, barite, pyrite, galena, chalcopyrite and tetrahedrite-tennantite, with very minor amounts of bornite and pyrrhotite. Clastic textures are common in
the ores. Textural relationships define four stages, including two substages, of mineralization (Stages 1, 2a, 2b, 3a, 3b and 4). Stage 1 is characterized by fine-grained minerals, framboidal and colloform pyrite, and mineralogical banding. Stage 2a consists of open space filling pyrite, sphalerite and barite, and recrystallized Stage 1 mineralization. Stage 2a sphalerite is weakly diseased with chalcopyrite. Stage 2b is dominated by coarsely-crystalline, open space filling pyrite and heavily chalcopyrite-diseased sphalerite. Stage 3a occurs in samples dominated by Stage 2a mineralization, and consists of galena, chalcopyrite and tetrahedrite-tennantite which both replace and fill open spaces in preexisting mineralization. Stage 3b is dominated by chalcopyrite, which pervades and replaces all previous sulfide mineralization. Stage 4 consists of barite which fills cavities dissolved in ore of the previous three stages.

20. Thermochemical data suggest that $\Sigma S_{\text{O}_4}^-$ contents of Stage 2a and Stage 3a fluids were $10^{-3}$ and $10^{-5}$ to $10^{-6}$ m, respectively, and $H_2S$ contents were approximately $10^{-3.5}$ and $10^{-4.5}$ to $10^{-5}$ m, respectively. The activity of oxygen and $SO_4^-/H_2S$ ratio of the hydrothermal fluids remained constant or decreased somewhat in fluids from Stage 2a to Stage 3a, while total sulfur contents decreased.

21. The salinities of fluids which deposited open space filling quartz within Type 1 zones ranged from 3.5 to
12.3 equivalent weight per cent NaCl. Temperatures of the fluids were between 240 and 260°C.

22. The salinity of fluids which deposited grey barite in Type 1 zones ranged from 4 to over 10 equivalent weight per cent NaCl.

23. The $\delta^{34}$S values of syngenetic and epigenetic barites range from 12 to 23 per mil. The lower values reflect mixing of unmodified seawater sulfate with hydrothermal fluids, while the higher values indicate a deep-seated hydrothermal source. The two sulfate sources mixed close to the seawater-seafloor interface.

24. Ore-proximal epigenetic pyrites have $\delta^{34}$S values of $+1 \pm 2$ per mil. Syngenetic ore sulfides have $\delta^{34}$S values of $-15.8$ per mil in a sample of Stage 1 pyrite, $-6.4$ to $-1.6$ per mil in Stage 2a sphalerite, $-0.6$ to $+1.1$ per mil in Stage 2b sphalerite and pyrite, and $+3.0$ per mil in a sample of Stage 3a galena.

25. Isotopic temperatures from both epigenetic and syngenetic sulfate-sulfide pairs range from 250 to 340°C.

26. It is unlikely that partial equilibration of aqueous sulfur species within the mound environment in mixtures of unmodified seawater and hydrothermal fluids produced the relatively low isotopic values which characterize Stage 2a sulfides.
27. Stage 1 sulfides incorporated at least some biogenic sulfur. The source of sulfur in Stages 2 and 3 and in epigenetic mineralization is unconstrained.

28. Seawater was a component of the hydrothermal system, both as a deep-seated source (pore water) and as an endmember in mixing reactions close to the seawater-seafloor interface. Magmatic fluids may have supplied additional components to the hydrothermal fluids, including silica, salt and sulfur.

29. The geological characteristics of the Bully Hill area ore deposits are remarkably similar to those of the Miocene Kuroko deposits of Japan.
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