Base- and Precious-Metal Concentrations of Early Proterozoic Massive Sulfide Deposits in Arizona—Crustal and Thermochemical Controls of Ore Deposition

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Base- and Precious-Metal Concentrations of Early Proterozoic Massive Sulfide Deposits in Arizona—Crustal and Thermochemical Controls of Ore Deposition

By Ed DeWitt
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Base- and Precious-Metal Concentrations of Early Proterozoic Massive Sulfide Deposits in Arizona—Crustal and Thermochemical Controls of Ore Deposition

By Ed DeWitt

ABSTRACT

Of the 70 known Early Proterozoic massive sulfide deposits and prospects in Arizona, 48 have production data that can be used to infer differences about the origins of the various deposits. Thirteen massive sulfide metallic mineral districts contain 48 mines and prospects that, from 1884 through 1978, produced 55.3 million tons of ore containing 3.99 billion lb of Cu, 237 million lb of Pb, 1.0 billion lb of Zn, 75.2 million oz of Ag, and 2.0 million oz of Au. Average produced grades were 3.6 percent Cu, 0.2 percent Pb, 0.9 percent Zn, 1.36 oz/ton Ag, and 0.037 oz/ton Au. Because Pb and Zn were recovered only sporadically, in-situ grades of any deposit that contained Pb and Zn are higher than the averages indicated by the production figures above, about 0.5 percent Pb and 3–10 percent Zn. Ag/Au ratios for all deposits averaged 37, but ranged from 8 to 462 for deposits producing more than 20,000 tons of ore. Precious-metal concentrations ranged from less than 0.001 to 0.12 oz/ton for Au and from 0.009 to 3.56 oz/ton for Ag in deposits that produced more than 20,000 tons of ore.

Low-Au, low-Ag ore of the Hualapai and Old Dick districts contrasts markedly with the average for districts in the Prescott-Jerome area. These differences were likely caused by regional variations in the crust underlying western Arizona. Mojave-type crust, characterized by elevated \(^{207}\text{Pb}/^{206}\text{Pb}\) and Th/U values compared to central Arizona, underlies western Arizona and was partially melted to form much of the metavolcanic strata that host massive sulfide deposits in the Hualapai and Old Dick districts. Apparently, Early Proterozoic Mojave-type crust is impoverished in precious metals compared to the crust underlying central Arizona.

Younger (post-1,730 Ma and Phanerozoic) vein deposits in central and western Arizona formed largely in plutonic rocks that intruded Mojave-type crust. These deposits are characteristically gold-rich and have low Ag/Au values. This metallogenic signature is probably a crustal-scale phenomenon related to emplacement of voluminous plutons from 1,690 to 1,740 Ma that largely obliterated the metallogenic characteristics of the Early Proterozoic Mojave-type crust.

Low-Cu, high-Pb ore of the Big Bug district contained the highest precious metal concentrations, Au averaging 0.075 oz/ton and Ag averaging 2.65 oz/ton. Small deposits having metal ratios similar to the average for the Big Bug district are present in the Old Dick, Verde, and Agua Fria districts, and their presence indicates that local thermochemical controls of ore deposition, not regional factors, were important in the localization of these massive sulfide deposits that contain elevated precious-metal concentrations. Deposition of ore minerals at temperatures below 300°C from a sulfur-rich hydrothermal fluid is the most likely cause for the enhanced precious-metal concentrations, not formation of the deposits in a setting distal from volcanism.

Low-Au, low-Ag ore, locally present in the Agua Fria and Verde districts, also contrasts markedly with the average for districts in the Prescott-Jerome area. A likely cause of this depletion in precious metals is deposition of ore minerals in these deposits from hydrothermal fluids having temperatures in excess of 300°C, a temperature too high for most chloride and sulfide complexes to transport large concentrations of gold and silver in solution. Deposits of this type appear to have formed within rhyolite flows and tuffs, not at the contact of felsic and more mafic rocks.

INTRODUCTION

Early Proterozoic massive sulfide deposits associated with submarine mafic to felsic metavolcanic rocks are present throughout central, west-central, and northwestern Arizona (Anderson and Guilbert, 1979; DeWitt, 1983, 1987; Keith and others, 1983, 1984; Conway and Silver, 1986; Eastoe and others, 1987; Donnelly and Conway, 1988; Lindberg, 1989). Production data for copper, lead, zinc, gold, and silver (Arizona Geological Survey, unpub. data, 1992) for most of the known deposits and prospects in 13 metallic mineral districts (Welty and others, 1985) are summarized here. Nine of the thirteen districts have recorded production; only the Gray’s Gulch and Bronco Creek districts southeast of
EARLY PROTEROZOIC MASSIVE SULFIDE DEPOSITS IN ARIZONA

Figure 1. Map of central and northwestern Arizona showing location of Early Proterozoic massive sulfide metallic mineral districts.

Payson and the Pittsburg-Tonto and Pranty's Cabin districts south of Payson (fig. 1) lack data and are not discussed. These four districts produced little ore; omission of their production totals does not materially affect the trends noted for the area shown on figure 1. Production data for the remaining nine districts, which contain 48 mines for which metal data are available, allow trends in metal content and metal ratios from mine to mine and district to district to be evaluated. Some of these trends were noted by DeWitt (1983) and Lindberg (1989).

Data used in this paper have been thoroughly checked for accuracy and completeness; however omissions are probably the most likely source of error. Small mines and deposits are particularly likely to have incomplete production records, as are many mines that operated in the late 1800's and earliest 1900's. Metal contents, ratios, and trends are most reliable for large mines and those having complete and verifiable records. Some published production data for massive sulfide deposits in Arizona disagree with the data summarized here (examples are the Iron King Mine in the Big Bug district (Gilmour and Still, 1968) and some of the notes in Donnelly and Conway, 1988); data summarized in this paper should supersede earlier summaries. Rigorous statistical treatment of the production data is not deemed appropriate, as ore types have been somewhat homogenized by the reporting of amounts of ore and metals on a yearly basis.

This in-depth comparison of metal ratios and concentrations based on production records is valid, primarily, because all the massive sulfide deposits were mined by the same underground techniques, and similar base and precious metals were extracted throughout the lifetimes of the mines. Milling techniques were similar from deposit to deposit, and smelting procedures, recoveries, and returns were similar due to the small number of smelters operative during the lifetime of most mines. Therefore, different mining techniques did not result in widely different dilution rates for stratabound ores. Only the largest mine, the United Verde (Verde district), experienced changes in smelter technology; those changes are reflected in the production data. Also, except where noted, yearly production grades for various metals approximate the in-situ concentrations of ore zones. Average production grades, especially for lead and zinc, may or may not reflect in-situ concentrations, as some metals were not produced throughout the lifetime of various mines.

DISTRIBUTION, AGE, AND CHARACTERISTICS OF DEPOSITS

Metavolcanic rocks of basaltic to rhyolitic composition are host to numerous Early Proterozoic, syngenetic, massive sulfide deposits in central Arizona. Although most of the
deposits are in the Prescott-Jerome region of central Arizona, mines and prospects are noted from the northwestern part of the state to the east-central part of the state (fig. 1). The deposits are within 1,700- to 1,780-Ma metavolcanic strata. All deposits in the Prescott-Jerome area are hosted by 1,740- to 1,780-Ma mafic to felsic metavolcanic strata (Anderson and others, 1971; Anderson and Silver, 1976; Anderson, 1978, 1987, 1989a,b; Donnelly and Hahn, 1981; Bowring and others, 1986; Karlstrom and others, 1987). Deposits in the western part of the state (Hualapai and Old Dick districts) are in mixed metavolcanic and metasedimentary strata that are about 1,730 Ma (Silver, 1968; Bryant and Wooden, 1986; Chamberlain and Bowring, 1990; Wooden, unpub. data, 1990). These deposits near Payson are associated with felsic to mafic metavolcanic strata that are 1,700–1,730 Ma (Gastil, 1958; Ludwig, 1973; Conway, 1976; Silver and others, 1986; Conway and Karlstrom, 1986; Karlstrom and others, 1990). Massive sulfide deposits are associated neither with Early Proterozoic, predominantly subaerial, felsic metavolcanic rocks (Wilson, 1939; Conway, 1976; Conway and Silver, 1989) that are younger than 1,700 Ma nor with the pelitic and psammitic Pinal Schist of southeastern Arizona.

Some deposits, such as the United Verde, Bruce and Old Dick, and to a lesser extent the Stoddard and Antler, have the classic features associated with submarine, volcanogenic deposits (Hutchinson, 1973; Franklin and others, 1981): stratabound nature, massive sulfide ore at the top of a major rhyolite body, zonal arrangement of metals within the deposit, and chloritic alteration pipe beneath the deposit. Others, such as the Iron King, Bluebell, Copper World, and Kay, appear to lack recognizable chlorite alteration pipes and metal zonation within the deposits, and instead include extensive areas of sericite-rich rocks and minor chlorite-rich rocks. Some, such as the Huron, Swindler, and Orizaba, have alteration pipes characterized by aluminosilicate-rich rocks and epidote (O’Hara, 1987a; DeWitt, unpub. data, 1989; O’Hara and Long, 1991).

Some deposits have been studied in detail, principally the Iron King Mine, in the Big Bug district (Gilmour and Still, 1968, and references cited therein); the Bruce Mine, in the Old Dick district (Baker and Clayton, 1968; Larson, 1984 and references cited therein); the United Verde Mine, in the Verde district (Anderson and Creasey, 1958; Lindberg, 1986c, 1989; DeWitt and Waegli, 1989; Gustin, 1990), and the United Verde Extension Mine, in the Verde district (White, 1986a). Others, principally the Copper Queen Mine, in the Agua Fria district (Brook, 1974); the Antler and Copper World Mines, in the Hualapai district (Romslo, 1948; More, 1980); and the Copper Chief Mine, in the Verde district (Johnson, 1986b; Lindberg, 1986b), have been investigated in less detail. Many, however, have not been mapped or sampled since Lindgren’s (1926) report on mines in the Prescott-Jerome region. This summary paper and previous summaries (Anderson and Guilbert, 1979; DeWitt, 1983; Lindberg, 1989) reveal trends in metal concentrations that were caused by first-order crustal differences and second-order thermochemical conditions of ore deposition. Obviously, additional work is needed on most deposits before they will be more fully understood.

OVERALL DISTRICT SUMMARY

The 48 massive sulfide deposits in Arizona for which production data are available produced 55.3 million tons of ore that contained 3.99 billion lb of Cu, 237 million lb of Pb, 1.02 billion lb of Zn, 75.2 million oz of Ag, and 2.06 million oz of Au (table 1). From all districts, ore averaged 3.6 percent Cu, 0.2 percent Pb, 0.9 percent Zn, 1.35 oz/ton Ag, and 0.037 oz/ton Au. Averaged lead and zinc grades are artificially low, as most mines did not produce lead- and zinc-rich ore because they were penalized at the smelter for zinc. Lead, when produced, normally averaged less than 0.5 percent except for deposits in the Big Bug district. Zinc, when produced, averaged 3–10 percent. Copper, silver, and gold grades most accurately reflect the metal concentrations of the deposits because these metals were always profitably extracted. However, even gold and silver grades could have been partly biased if precious-metal-rich parts of various deposits were not mined because they were zinc-rich. Therefore, the combined Cu-Pb-Zn content of most deposits averaged about 7 percent, but was poor in lead. Silver/gold ratios averaged 37 but varied from 183 for the Old Dick district to 12 for the Zonia district.

Of the nine massive sulfide districts for which production data are available, the Verde district produced by far the most ore and metals (table 1). Sixty-nine percent of the ore, 93 percent of the Cu, 74 percent of the Ag, and 73 percent of the Au were produced from this district. The United Verde Mine, the third largest massive sulfide deposit in North America (DeWitt and Waegli, 1989; Lindberg, 1989) produced almost 90 percent of the ore from the district. Copper grade for the district (4.91 percent) is higher than the overall average primarily because of the extremely rich copper ore of the United Verde Extension Mine, which averaged 10 percent Cu. The Verde district also could have led all districts in zinc production (McIlroy and others, 1974), but the zinc-rich part of the United Verde deposit has not been mined (Anderson and Creasey, 1958; DeWitt and Waegli, 1989).

The Zonia district produced the second largest amount of ore, but much of this was by open-pit mining and heap leaching of low-grade copper during the 1970’s. Because most other deposits were not mined by open-pit operations (some ore from the United Verde being an exception), raw production totals from the Zonia district cannot be reasonably compared to those of other districts. The low Ag/Au value (12) for the Zonia district is also biased because, during open-pit operations, data for gold and silver were not
Table 1. Production data for metallic mineral districts and massive sulfide deposits, Arizona.

[Data from Arizona Geological Survey, unpub. data, 1992: Cu, copper; Pb, lead; Zn, zinc; Ag, silver; Au, gold; t, short tons; lb, pounds; oz, Troy ounces; oz/t, Troy ounces per short ton; --, no record of production for that element; 0.00x grade of element is less than 0.000999; 0.00x, grade of element is less than 0.0000999; copper, silver, and gold amounts and grades accurately reflect metal concentrations and ratios in the massive sulfide deposits because these metals normally were produced throughout mining of the deposit; lead and zinc amounts and grades, in most instances, do not accurately reflect concentrations and ratios in the deposits because lead and zinc seldom were produced throughout the lifetime of the deposit. See text for ratios that are closer to actual]
<table>
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<th>Cu (lb)</th>
<th>Pb (lb)</th>
<th>Zn (lb)</th>
<th>Ag (oz)</th>
<th>Au (oz)</th>
<th>Cu (%)</th>
<th>Pb (%)</th>
<th>Zn (%)</th>
<th>Ag (oz/t)</th>
<th>Au (oz/t)</th>
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<td><strong>801</strong></td>
<td><strong>4,019</strong></td>
<td><strong>340</strong></td>
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<td><strong>0.000</strong></td>
<td><strong>0.000</strong></td>
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recorded. Therefore, for massive sulfide districts mined by underground methods, the lowest Ag/Au value (18) for the Kay district should be considered more representative than the figure for the Zonia district.

The Big Bug district, and principally the Iron King Mine, produced the third largest amount of ore but the most lead (98 percent of the total) and zinc (60 percent of total). The district is unusual because of its low copper grade (0.11 percent), high lead (almost an order of magnitude higher than any other district), and high precious metals (gold and silver grades are a factor of 2 higher than most other districts).

The Old Dick district produced the fourth largest amount of ore, but had the highest zinc grade (9.06 percent). The zinc-rich nature of deposits in the district is real and not an artifact of production during World War II, the Korean War, and the 1970's. The district has the second lowest silver grade and the lowest gold grade, except for the Zonia district, as noted above. As a result, the Ag/Au of 183 is the highest of any district in the state and is markedly different from all districts in the Prescott-Jerome area. The precious-metal-poor nature of the Old Dick district and Hualapai district is discussed in the following section on tectonic setting of deposits.

Mines in the Mayer district produced the third largest amounts of copper, silver, and gold, and had the second lowest Ag/Au value (25). Deposits in the district were zinc-poor and had undetermined, though minor, amounts of lead.

The remaining districts (Agua Fria, Hualapai, Kay, and New River) produced minor amounts of ore but had some distinctive metal ratios. Agua Fria, dominated by production from the Binghampton Mine, had anomalously low silver and gold grades (0.261 oz/ton and 0.005 oz/ton, respectively) for a district in the Prescott-Jerome area. Hualapai had the second lowest lead grade and the second lowest Ag/Au (148). Kay, although producing only a few thousand tons of ore, had the lowest Ag/Au, 18 (Zonia excluded). New River's low gold and silver grades are partially a function of missing production data.

Compared to other massive sulfide deposits of Archean, Early Proterozoic, and Phanerozoic age, averages and ranges of base- and precious-metal concentrations in Arizona deposits are comparable to Archean deposits in Canada (Hutchinson, 1973; Sangster, 1980; Franklin and others, 1981), Paleozoic deposits in the Appalachian region of the United States and Canada (Sangster, 1984), Paleozoic deposits in eastern Australia (Large and others, 1989), Tertiary deposits in Japan (Ishihara, 1974; Ohmoto and Skinner, 1983), and Recent deposits on various mid-ocean ridges (Bischoff and others, 1983; Koski and others, 1984, 1985; Hannington and others, 1986; and Hannington and Scott, 1989b).

**SUMMARY OF MINES BY DISTRICT**

Many mines lack sufficient production data to draw reliable interpretations concerning metal concentrations. In this category are mines that either produced less than about 20,000 tons of ore, had production data for fewer than 5 years, or had highly variable grades from one year to the next. Data for those deposits are summarized in Table 1, but detailed discussions of those deposits' geologic setting and metal ratios are not attempted, except to clarify features of the production data that are not obvious from inspection of the cumulative totals. Most mines that produced more than 20,000 tons of ore and reliable data are discussed in some detail, district by district.

**AGUA FRIA DISTRICT**

Located in the Prescott-Jerome area (Fig. 1), the Agua Fria district (Fig. 2) contains massive sulfide deposits that are largely restricted to metarhyolite flows and tuffs (Lindgren, 1926; Evensen, 1969, 1980; Anderson and Blacet, 1972b,c) Anderson and Guilbert, 1979; DeWitt, 1983, 1987; Anderson, 1986a; 1989a). The district is unusual for its low gold and silver grade. Although the silver grade is lower by a factor of 5 than in surrounding districts, the gold grade is lower by an order of magnitude (Table 1).

At the Binghampton Mine (Lindgren, 1926; Higgins, 1986), ore is localized within a large metarhyolite-dacite unit. Chalcopyrite-tetrahedrite is the predominant ore assemblage. As the largest producer in the district (Table 1), the deposit is the principal factor causing the low grades of precious metals over the lifetime of the mine, Ag/Au is rather constant (Table 1, fig. 3), which indicates that the low grades of precious metals are not an artifact of poor data. Also, the positive correlation of copper and silver indicates that, in general, the production data are not flawed for the Binghampton Mine. The positive correlation of copper and silver is probably due to the presence of tetrahedrite. Apparently, the Agua Fria district, characterized by the Binghampton deposit, is a precious-metal-poor region within the otherwise average to precious-metal-rich Prescott-Jerome area.

The Stoddard Mine (Lindgren, 1926), the second largest producer in the district, is localized within a large metarhyolite unit. The deposit shows a modest correlation of gold with silver and a good correlation of copper with silver (Fig. 4). Silver grade at the Stoddard is as low as the Binghampton, but gold grade is notably higher (0.023 compared to 0.001 oz/ton). However, this higher grade may be an artifact of more enriched, oxidized ore in a smaller deposit (Table 1). Although lead and zinc grades appear low for the Stoddard, when lead and zinc were produced, their grades were 0.7-5.0 percent for lead and 3-30 percent for zinc.

The Copper Queen Mine (Lindgren, 1926; Brook, 1974; Higgins, 1986; Hurlbut and others, 1986), the third
SUMMARY OF MINES BY DISTRICT

largest producer in the district and located adjacent to the Binghampton Mine (fig. 2), appears from table 1 to be much richer in precious metals than is the Binghampton. Ore at the Copper Queen is localized in the same metarhyolite-dacite unit and contains the same minerals. Data for the Copper

Queen are highly influenced by approximated data for 1901; without that data the deposit averaged ~0.6 oz/ton Ag and ~0.06 oz/ton Au, values that are more similar to the Binghampton. When zinc was produced at the Copper Queen, it averaged 3.8 percent.

Unusual deposits for the district include the Pocahontas (Lindgren, 1926; Evensen, 1969), with 1.7 percent Pb and only 0.27 percent Cu, and 0.13 oz/ton Au. The Stoddard produced a minor amount of lead-rich ore, so the high lead concentration for the Pocahontas, especially considering the minor amount of ore produced, may not be highly significant. Metal ratios in the Pocahontas are similar to those in the Iron King and Hackberry Mines, in the Big Bug district.

BIG BUG DISTRICT

The Big Bug district is northwest of the Agua Fria district (figs. 1 and 5) and is characterized by massive sulfide deposits spatially associated with one metarhyolite tuff that is overlain and underlain by metabasalt (Lindgren, 1926; Creasey, 1950, 1952; Gilmour and Still, 1968; Anderson and Blacet, 1972b; Bouley and Hodder, 1976; Webb, 1979; Anderson and Guilbert, 1979; DeWitt, 1983, 1987; Anderson, 1986a, 1989a; O’Hara, 1986; O’Hara and Armstrong, 1986). The district has the lowest copper grade and the highest lead, silver, and gold grades of any district (table 1). Although production from the district is highly biased by the Iron King Mine (table 1), which accounted for 99 percent of the ore, 94 percent of the copper, and 99 percent of the precious metals, all the small deposits (fig. 5) have silver grades of 1–4 oz/ton and gold grades of 0.1–0.4 oz/ton. Likewise, except for the Butternut and Lone Pine, all copper grades for small mines are less than 2 percent. Therefore the district as a whole is poor in copper and rich in lead, silver, and gold. Zinc, when produced, was average compared to most districts. Cambrian lead- and gold-rich massive sulfide deposits in western Tasmania bear a striking resemblance to those in the Big Bug district (Large and others, 1989).

The copper-poor and lead-, silver-, and gold-rich deposit at the Iron King Mine is localized along altered metarhyolite units within a metabasaltic to andesitic flow sequence (Lindgren, 1926; Mills, 1941, 1944, 1946, 1947; Hendricks, 1947; Creasey, 1950, 1952; Kumke and Mills, 1950; Anderson and Creasey, 1958; Mitchell, 1964; Gilmour and Still, 1968; Lawrence and Dixon, 1986). Two ore horizons are present, a lower copper- and zinc-rich zone, and a higher copper-poor zone (Lindberg, 1989). Ore minerals are sphalerite, galena, pyrite, tennantite, arsenopyrite, and chalcopyrite. Production data for the nine reveal moderate correlation of copper with gold (fig. 6) and copper with silver (fig. 7), but a much better correlation of lead with gold (fig. 6), especially for gold grades less than 0.1 oz/ton. Data points that lie to the lower right of the major positive correlation of
gold and lead—those having high precious-metal concentrations and low lead concentrations—come from pre-1940 production (fig. 8) in which oxidized(?), anomalously gold- and silver-rich ore having unusually low base-metal concentrations was mined. Elimination of those points from figures 6 and 7 strengthens the positive correlation of precious metals, especially gold with lead (fig. 8). Variations in Ag/Au are caused more by shifts in gold grade than shifts in silver grade (fig. 9), which remained essentially constant from 1940 to 1970 (fig. 10). Creasey (1952) and Gilmour and Still (1968) suggested that silver is present in tennantite, but metallurgical tests have not proven that association. Both authors state that gold appears to be associated with pyrite, galena, and sphalerite. However, the production data (fig. 6) show that much gold is spatially associated with galena. Neither precious metal correlates well with zinc but, importantly, high zinc grades do not indicate low precious-metal concentrations (figs. 6 and 8).

The Hackberry Mine (Lindgren, 1926), the second largest producer in the district, is also rich in lead, silver, and gold (table 1). The deposit is localized at the contact of metarhyolite and metabasalt and is probably at the same stratigraphic position as the Iron King Mine to the north. Correlation of this metarhyolite horizon, which hosts most of the massive sulfide deposits in the Big Bug district (Anderson and Blacet, 1972a,b) is strengthened by the similarity of metal ratios in mines along the horizon. Pyrite-chalcopyrite-galena-sphalerite-tetrahedrite is the ore assemblage. Ag/Au for most of the lifetime of the mine has been rather constant (fig. 11). Silver correlates very well with lead, but less well with zinc (fig. 11), and probably indicates that precious metals are mostly associated with galena. Lead and zinc, when produced, averaged 2.37 percent and 5.25 percent, respectively for the deposit.

Smaller mines in the district have several noteworthy features. Totals for the Butternut are highly influenced by

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**Figure 3.** Plot of silver vs. gold and copper in the Binghamton Mine, 1916-47. Symbols that plot on the x-axis indicate no data for gold, not values of zero.

**Figure 4.** Plot of silver vs. gold and copper in the Stoddard Mine, 1929-57. Symbols that plot on the x-axis indicate no data for gold; symbols that plot on the y-axis indicate no data for silver.
SUMMARY OF MINES BY DISTRICT

R.1 W. R.1 E. SCALE 1:100 000

0 2 MILES

Figure 5. Location map of mines in the Big Bug district. Base from U.S. Geological Survey, Bradshaw Mountains and Prescott 1:100,000, 1981. Mine names in italics are massive sulfide deposits for which production data are not available. Data for 1903, which account for half the total ore produced and much of the very high grade material. Data for the Lone Pine include high-grade lead and silver ore for 1924, which may not be entirely representative of most ore in the mineralized system. The Boggs Mine (Hurlbut, 1986) is one of the highest grade deposits for precious metals in the area. The Huron and Swindler (or Victor-Swindler) prospects (O'Hara, 1987a; O'Hara and Long, 1991) are characterized by extensive alumino-silicate assemblages and development of quartz-epidote in the footwall of the massive sulfide deposits. Their somewhat unusual alteration assemblages may indicate slightly different physico-chemical conditions of formation compared to surrounding deposits.

The Bell Ranch prospect (Swan and others, 1981; Swan, 1987; O'Hara, 1987b), located southeast of the Lone Pine Mine, has produced no ore, but is similar in most regards to other mines in the Big Bug district. Gold- and silver-bearing pyrite, chalcopyrite, and arsenopyrite are present in and adjacent to metahyotlite. Very little massive sulfide ore is known. The Bell Ranch prospect may be a gold-rich end member of the precious-metal-rich deposits in the Big Bug district.

In summary, for the Big Bug district, the highest precious-metal grades are in deposits having the highest lead concentrations. The district as a whole is very lead-rich and has the highest silver and gold grades in the state. The Ag/Au of 35, which is the same as the state average, indicates that the district is preferentially enriched in both precious metals, and suggests that gold and silver are spatially associated with galena in the deposits.

HUALAPAI DISTRICT

The Hualapai district (Anderson and Guilbert, 1979; More, 1980; Stensrud and More, 1980; Loghry and Heinrichs, 1980; DeWitt, 1983, Conway and others, 1990), in the central Hualapai Mountains of northwestern Arizona (figs. 1 and 12), is unusual compared to districts in the Prescott-Jerome area because of its high Ag/Au (148) and its low precious-metal concentrations, especially gold (table 1), which are among the lowest in the state. Massive sulfide deposits at the Antler Mine are localized in thin metavolcanic units that are overlain and underlain by pelitic, metasedimentary rocks and at the Copper World Mine are within the pelitic rocks. Therefore, the tectonic setting of the deposits is fundamentally different from those in the Prescott-Jerome area, which are entirely within thick metavolcanic sequences.

The Antler Mine is localized in felsic gneiss and amphibolite that is interbedded with pelitic metasedimentary rocks (Romslø, 1948; More, 1980; Stensrud and More, 1980; Conway and others, 1990). Ore minerals include iron-rich sphalerite, chalcopyrite, galena, pyrrhotite, and pyrite. Production data from the mine, the largest producer in the district, reveal that the deposit has a relatively constant Ag/Au and that silver (and consequently gold) correlates best with copper and less well with lead (fig. 13). Zinc does not correlate well with precious metals, but high zinc grades do not mean depressed gold or silver grades. Assay data (Romslø, 1948) show that silver correlates best with lead and less well with combined lead and zinc. Silver correlates poorly with copper. Data for 1948 suggest that an unusual ore type was mined from the deposit that year. When produced, lead and zinc averaged 0.40 percent and 3.45 percent, respectively. The existence of both pyrrhotite and iron-rich sphalerite at the Antler is noteworthy. Whether or not pyrrhotite is primary or the result of contact metamorphism cannot be determined from present data.

The Copper World Mine is hosted by pelitic to psammitic metasedimentary rocks (More, 1980; Stensrud and
Figure 6. Plot of gold vs. copper, lead, and zinc in the Iron King Mine, 1903–69. Symbols that plot on the x-axis indicate no data for copper or zinc.

Figure 7. Plot of silver vs. copper, lead, and zinc in the Iron King Mine, 1903–69. Symbols that plot on the x-axis indicate no data for lead or zinc.

Figure 8. Plot of year of production vs. gold, lead, and zinc in the Iron King Mine, 1936–69. Symbols that plot on the x-axis indicate no data for zinc.
SUMMARY OF MINES BY DISTRICT

Figure 9. Plot of year of production vs. Ag/Au, silver, and gold in the Iron King Mine, 1936-69.

Figure 10. Plot of year of production vs. ore, silver, and gold in the Iron King Mine, 1936-69.

Figure 11. Plot of silver vs. gold, lead, and zinc in the Hackberry Mine, 1905-56. Symbols that plot on the x-axis indicate no data for gold, lead, or zinc.
More, 1980). Ore minerals include sphalerite, chalcopyrite, galena, pyrite, and pyrrhotite. The deposit has relatively constant Ag/Au, but precious metals do not correlate very well with any base metal (fig. 14). Because lead and zinc were recovered for most years for which production data are available, the grades in table 1 accurately reflect metal concentrations of the deposit. Only the Binghamton Mine in the Agua Fria district and the Old Dick Mine in the Old Dick district have gold grades lower than in the Copper World Mine.

**KAY DISTRICT**

The Kay district, located south of the Agua Fria district (figs. 1 and 16), is characterized by small massive sulfide deposits in a large complex of metarhyolite tuff and minor meta-andesite (Willis, 1920b; Lindgren, 1926; Jerome, 1956; Anderson and Guilbert, 1979; Winn, 1982; DeWitt, 1983, 1987; Anderson, 1989a). The district has the lowest Ag/Au (18, Zonia excepted), and the second highest gold grade in the state. Because the district produced only 2,500 tons of ore (table 1), these figures may not be representative of metal ratios for all deposits in the district.

Data from only the Kay Mine (Willis, 1920a, 1924; Anonymous, 1919, 1924, 1925, 1926; Southwest Mining News Service, 1925; Lindgren, 1926; Jerome, 1956) can be reliably interpreted. The deposit is localized near the contact of metarhyolite and metabasalt. Ore minerals are pyrite, chalcopyrite, galena, minor tetrahedrite-tennantite, and arsenopyrite. Ag/Au during the life of the mine was constant (fig. 15). Gold and silver correlate moderately well with copper. Lead, when produced, averaged 2.2 percent. Gold may be spatially associated more with galena than with tetrahedrite-tennantite, as at the Iron King Mine, but data for lead are too sparse to be sure.

**MAYER DISTRICT**

Located southwest of the Agua Fria district, the Mayer district (figs. 1, 17) contains massive sulfide deposits in and at the contacts of metarhyolite flows with metabasalt and meta-andesite (Lindgren, 1926; DeWitt, 1976, 1978, 1979, 1987; Anderson and Guilbert, 1979; O'Hara, 1980; Vrba, 1980; Argenbright and Karlstrom, 1986; Anderson, 1989a). The district has average to very slightly low copper and silver grades and an average to slightly high gold grade (table 1). Two mines, the Bluebell and DeSoto (table 1), produced all the ore from the district and have very similar metal concentrations. Neither produced lead or zinc, and both contain only minor galena or sphalerite (Lindgren, 1926).

The Bluebell Mine was the fifth largest massive sulfide deposit in the state in terms of tons of ore produced. The deposit is localized in and at the contact of underlying metabasalt and overlying metarhyolite (Lindgren, 1926; DeWitt, 1976, 1979). Both pyrite-rich and pyrite-poor ore is present. Ore minerals are pyrite, chalcopyrite, minor arsenopyrite, sphalerite, and minor galena. Gold correlates well with silver (fig. 18), resulting in a constant Ag/Au of about 25 over much of the life of the mine. High gold and silver grades after 1920 are a result of mining small quantities of enriched ore (fig. 18). The prominent peak for 1905 data is a result of estimating pre-1905 production. Silver and gold correlate well with copper (fig. 19).

The DeSoto Mine (Lindgren, 1926; Blacet, 1968; DeWitt, 1976, 1979; Vrba, 1980) produced only one-fourth as much ore as the Bluebell, but shared most of its characteristics. Massive sulfide and stringer ore are at the contact of underlying metabasalt and overlying metarhyolite. Ore minerals are the same as at the Bluebell Mine. Gold correlates highly with silver (fig. 20). Ag/Au is constant over the lifetime of the mine. Silver (and hence, gold) correlates moderately well with copper (fig. 21). A 1904 estimate accounts for half the ore produced at the DeSoto, but that estimate agrees with metal ratios for succeeding years.

**NEW RIVER DISTRICT**

The New River district, southeast of the southernmost part of the Kay district (figs. 1, 22), contains only one mine,
SUMMARY OF MINES BY DISTRICT

Figure 13. Plot of year of production vs. silver, copper, and lead in the Antler Mine, 1943–61.

Figure 14. Plot of year of production vs. gold, copper, zinc, and lead in the Copper World Mine, 1944–54. Symbols that plot on the x-axis indicate no data for lead or gold.

Figure 15. Plot of gold vs. copper and silver in the Kay Mine, 1910–66. Symbols that plot on the y-axis indicate no data for copper or silver.
Figure 16. Location map of mines in the Kay district. Base from U.S. Geological Survey, Bradshaw Mountains 1:100,000, 1981. Mine names in italics are massive sulfide deposits for which production data are not available. A, northern part; B, southern part.

Figure 17. Location map of mines in the Mayer district. Base from U.S. Geological Survey, Bradshaw Mountains 1:100,000, 1981.

the Orizaba, localized in meta-andesite and metabasalt (Anderson and Guilbert, 1979; DeWitt, 1983, 1987; Maynard, 1986). Pyrite-chalcopyrite-minor sphalerite is the ore assemblage. On first inspection of table 1, the Orizaba appears to have an anomalously low gold grade (0.007 oz/ton). However, production records for gold from the mine are incomplete; when gold was reported, the Ag/Au was 24, not 64 as summarized in table 1, and gold averaged 0.01–0.02 oz/ton. This gold grade is slightly lower than in the Kay district to the west, but is in better agreement with districts farther north that contain similar massive sulfide deposits hosted in thick metavolcanic sequences. The minimal data for the Orizaba indicate that silver correlates moderately with gold and that both precious metals correlate moderately with copper (fig. 23). No data for lead or zinc are available.

OLD DICK DISTRICT

The Old Dick district, at Bagdad (figs. 1 and 24), is unusual because it has the highest average zinc grade (9.06
percent), the lowest gold grade (0.002 oz/ton), the highest Ag/Au (183), and the second lowest silver grade (0.387 oz/ton) (table 1). Averages for individual deposits were even more extreme: 16 percent Zn, 0.001 oz/ton Au, Ag/Au of 462, and 0.355 oz/ton Ag (table 1). These unusual metal ratios are dissimilar to those for mines and districts in the Prescott-Jerome area but are like those in the Hualapai district. The metavolcanic belt at Bagdad is relatively thin in comparison to those in the Prescott-Jerome area and is laterally not as extensive (Anderson and others, 1955; Baker and Clayton, 1968; Clayton and Baker, 1973; Mauger, 1973; Clayton, 1978; Larson, 1976, 1977, 1984, 1987; Douglas, 1982; Conway and others, 1986a,b; Connelly and Conway, 1983, 1987; Connelly and others, 1986). The deposit is localized at the top of the Bridle Formation, a sequence of metabasalt flows, within and at the base of the Dick Rhyolite, which is a metarhyolite dome and intrusive rock. Ore minerals are pyrite, sphalerite, chalcopyrite, galena, and cobaltian arsenopyrite. Sphalerite is both resinous and black (Anderson, 1950). Clean concentrates of sphalerite contain about 8 percent Fe (Baker and Clayton, 1968). Pyrrhotite is a common gangue. Initial
production from the Old Dick in the early 1940's consisted mainly of high-grade lead and zinc ore that averaged 2–4 percent Pb and 12–17 percent Zn. This ore had a Ag/Au of 50–150 and silver grades of 0.5 oz/ton (figs. 25, 26). As mining progressed, lead and zinc grades decreased (fig. 25), and gold grades decreased more dramatically than silver grades, resulting in an increase in the Ag/Au from about 150 in the early 1950’s to 250 at the close of mining operations. The Old Dick Mine has the dubious distinction of having the lowest gold grade (0.001 oz/ton) of any massive sulfide deposit in Arizona (table 1). From 1947 through 1966, gold correlated moderately with copper (figs. 25 and 26); copper and gold spikes in 1952 and 1954 may indicate dramatically different ore types being produced. Silver correlates highly with zinc and moderately with lead (fig. 25). All metal grades decreased as mining came to an end in 1966.

As the last of the Old Dick orebody was depleted, the deeper Bruce orebody was mined (Anonymous, 1973; Clayton, 1978). Ore minerals in the deposit are similar to those of the Old Dick with the exception of notable pyrrhotite and minor tennantite. During mining of the Bruce deposit, gold grades increased by a factor of 4, silver by a factor of 2, zinc by 50 percent, and copper by 20 percent compared to production from the Old Dick deposit. Data for lead are too incomplete for a meaningful analysis. A dramatic four-fold difference in gold grades between the two orebodies is noted. Silver in the Bruce Mine correlates well with both copper and zinc (fig. 27). Gold concentrations and elements that correlate with gold differ greatly from the Bruce to the Old Dick. These differences are probably caused by the copper- and zinc-rich zones in the body noted by Clayton (1978) and suggest zoning of gold within the deposit.

The Copper King Mine is localized in meta-tuffs within metabasaltic flows and is near the contact of an intrusive part of the overlying Dick Rhyolite (Anderson, 1950; Anderson
SUMMARY OF MINES BY DISTRICT

VERDE DISTRICT

The Verde district (fig. 32), produced by far the most ore and metals of any massive sulfide district in Arizona (table 1). Production was dominated by the 33.5 million tons of ore from the United Verde Mine. The United Verde Extension produced 39 million tons; no other deposit accounted for more than 400,000 tons of ore (table 1). The small deposits in the region are similar in most respects to the larger ones, but significant differences exist that are discussed below.

The largest mined volcanogenic massive sulfide deposit in the United States, the United Verde Mine at Jerome is one of the best studied deposits in Arizona if not in the entire United States (Reber, 1922, 1938; Lindgren, 1926; Anderson and Creasey, 1958, 1967; Anderson and Nash, 1972; Lindberg and Jacobson, 1974; DeWitt and Waegli, 1986, 1989; Lindberg, 1986a,c, 1989; Vance, 1987; Vance...
EARLY PROTEROZOIC MASSIVE SULFIDE DEPOSITS IN ARIZONA

Figure 23. Plot of silver vs. copper and gold in the Orizaba Mine, 1918–48.

Figure 24. Location map of mines in the Old Dick district. Base from U.S. Geological Survey, Bagdad 1:100,000, 1979, and Alamo Lake 1:100,000, 1979.

...and Condie, 1987; Gustin, 1988a, 1990; also, specific items of interest are in Graton, 1908; Provot, 1916; Finlay, 1918a,b; Rice, 1920; Smith and Sirdevan, 1921; Mills, 1925, 1934; Alenius, 1930, 1968; Barker, 1930; Hansen, 1930; Keefe, 1930; Lindgren, 1930; Ralston and Hunter, 1930; Slavin, 1930; Tenney, 1935; Pullen, 1943; Yeats, 1946; Storms, 1955; Kothavala, 1963; Nash, 1973; Stacey and others, 1976; Norman, 1977; DeWitt, 1983; Vance and Condie, 1985, 1986; Armstrong and Handverger, 1986; Gustin, 1986, 1987, 1988b; Lesher and others, 1986; Lindberg, 1986d; O’Hara and Armstrong, 1986; Eastoe and others, 1987; Lindberg and Gustin, 1987; Lindholm, 1989, 1991). The deposit is localized at the top of the lower part of the Cleopatra Member of the Deception Rhyolite, a very thick metarhyolite complex. Ore minerals are pyrite, chalcopyrite, sphalerite, galena, arsenopyrite, and minor tennantite. Base and precious metals in the deposit are zoned, from (1) a precious-metal-poor stringer zone at the base that contains only copper, through (2) overlying lenses of massive sulfide ore containing average copper, high zinc, and average precious metal concentrations, to (3) siliceous massive sulfide lenses containing average to high copper and zinc concentrations and average to high precious-metal concentrations, to (4) the capping chert and siliceous massive sulfide ore that contains lower copper and zinc concentrations, but the highest concentrations of precious metals (DeWitt and Waegli, 1989). This zonation is typical for those deposits in Arizona having well developed chlorite alteration pipes, stringer ore, and overlying stratiform lenses of massive sulfide ore.

During 87 years of production (fig. 33), gold grade consistently declined and Ag/Au increased. Most of the increasing Ag/Au through time is due to silver grades decreasing less than gold grades during that time (DeWitt and Waegli, 1989, fig. D2). Major mining terminated in 1953 (fig. 34); lower-than-average gold grades and higher-than-average...
Figure 25. Plot of year of production vs. silver, copper, zinc, and lead in the Old Dick Mine, 1947–66. Symbols that plot on the x-axis indicate no data for lead.

Figure 26. Plot of year of production vs. Ag/Au and gold in the Old Dick Mine, 1947–66.

Figure 27. Plot of year of production vs. silver, gold, copper, zinc, and lead in the Bruce Mine, 1968–77. Symbols that plot on the x-axis indicate no data for lead.
Figure 28. Plot of year of production vs. copper, lead, silver, and zinc in the Copper King Mine, 1917–27. Symbols that plot on the x-axis indicate no data for copper.

Figure 29. Plot of year of production vs. copper, lead, silver, and zinc in the Copper King Mine, 1942–52. Symbols that plot on the x-axis indicate no data for lead.

Figure 30. Plot of year of production vs. lead, zinc, and Ag/Au in the Copper King Mine, 1942–52. Symbols that plot on the x-axis indicate no data for lead.
SUMMARY OF MINES BY DISTRICT

Figure 31. Plot of year of production vs. silver, gold, copper, zinc, and lead in the Copper Queen Mine, 1960–66.

Ag/Au after 1953 are partially accounted for by leaching of high-grade copper ore during that period (fig. 34). Part of the peak in Ag/Au from about 1918 through 1924 (fig. 33) can be attributed to mining of low-grade gold ore during open-pit production (fig. 34). Some additional lowering of gold grade resulted from preferential mining of low-grade stringer ore both in the open pit and underground (P.A. Lindberg, written commun., 1993) compared to earlier and later time periods (fig. 33).

The United Verde was a copper-rich deposit (4.36 percent Cu) and had copper grades higher than other districts (all except the Kay district are less than 3.3 percent Cu; table 1). Silver and gold grades for the deposit are similar to the average for other districts (except Agua Fria) in the Prescott-Jerome area, but substantially higher than in the Old Dick and Hualapai districts. When recovered, zinc averaged 1–4 percent (fig. 35). However, much of the massive sulfide ore in the mine averaged 5–10 percent Zn, but this zinc-rich ore was not mined (McIlroy and others, 1974; DeWitt and Waegli, 1989, table 12). Data for lead grades are minimal; when produced, lead averaged 0.02 percent. Undoubtedly, the lead grade of much of the ore was higher.

Gold and silver grades are as high or higher in zinc-rich ore as in copper-rich ore at the United Verde (fig. 35). DeWitt and Waegli (1989, table 13) determined that the best statistical correlation of gold with base metals was with combined copper and zinc from siliceous massive sulfide ore (correlation coefficient of 0.61 for 14 samples) and combined massive sulfide and siliceous massive sulfide ore (correlation coefficient of 0.57 for 106 samples). No lead analyses were available to test the correlation of precious metals with lead.

The United Verde Extension Mine, which had the highest copper grade of any deposit in the state (10.2 percent Cu, table 1), also produced the second largest amount of copper
Figure 33. Plot of year of production vs. Ag/Au and gold in the United Verde Mine, 1884–1975. Symbols that plot on the x-axis indicate no data for Ag/Au.

Figure 34. Plot of year of production vs. ore and copper in the United Verde Mine, 1884–1975.

Figure 35. Plot of year of production vs. copper, zinc, silver, and gold in the United Verde Mine, 1940–53. Symbols that plot on the x-axis indicate no data for zinc.
and the third largest amounts of silver and gold (Rickard, 1918; Mitke, 1919; Lindgren, 1926; D'Arcy, 1930; Schwartz, 1937, 1938; Anderson and Creasey, 1958; Handverger, 1975; White, 1986a,b; Lindberg, 1989). The deposit is localized in metarhyolite thought to be equivalent to the lower part of the Cleopatra Member of the Deception Rhyolite. Ore minerals are chalcopyrite, tennantite, cuprite, and minor pyrite. Although the deposit was originally thought to be the downfaulted top of the United Verde deposit, recent workers consider the United Verde Extension to be a separate deposit (White, 1986a; Lindberg and Jacobsen, 1974; Lindberg, 1986a,c, 1989). Base- and precious-metal concentrations in the deposit are consistent with either interpretation.

Gold and silver grades in the United Verde Extension reveal that in its early history the deposit had anomalously high silver grades and low gold grades (fig. 36). The peak in silver grades correlates, in part, with exceptionally high-grade copper ore, exceeding 10 percent Cu (fig. 37). Silver was preferentially enriched in this chalcocite-rich material (Anderson and Creasey, 1958; White, 1986a). The peak in both silver and gold grades from 1936 through 1940 coincides with mining of the "gold stope," a chert-rich ore horizon at or slightly above the massive sulfide ore (Anderson and Creasey, 1958; White, 1986a,b; Lindberg, written comm., 1990).

Data for other mines in the Verde district exhibit some peculiar features. The anomalously high Ag/Au of 232 for the Cleopatra Mine and 419 for the Verde Central Mine (Willis, 1922; Benedict, 1923; Fearing and Benedict, 1925; Lindgren, 1926; Dickson, 1931; Reber, 1938; Anderson and Creasey, 1958) (table 1) are unusual. The Cleopatra ore is contained within the Cleopatra Member of the Deception Rhyolite, not at its top as is the United Verde ore. Semi-massive to massive sulfide ore of the Verde Central is beneath the Cleopatra Member (Lindberg, written comm., 1990). Ore minerals are only pyrite and chalcopyrite. In both cases, the high Ag/Au is a reflection of anomalously low gold grades recorded for fewer than three years of production data. These data could be wrong or incomplete or the deposits may be similar to other precious-metal-poor deposits in the Agua Fria district, especially the Binghampton and Copper Queen mines.

The Copper Chief (also known as "Iron King—Equator") Mine is localized at the top of a thin metarhyolite flow that overlies metabasalt flows (Lindgren, 1926; Reber, 1938; Anderson and Creasey, 1958; Rogers, 1979; Johnson, 1986a,b; Lindberg, 1986b). Ore minerals are pyrite, chalcocpyrite, galena, and minor sphalerite. The deposit has metal ratios similar to those at the Iron King and Hackberry mines, in the Big Bug district, and the Copper King Mine, in the Old Dick district. A low copper grade (0.39 percent average), moderate to high lead grade when produced (0.04–0.7 percent), and a high gold grade (0.13 oz/ton average; range from 0.3 to 0.7 oz/ton) for the Copper Chief are similar to metal ratios and concentrations of the Big Bug district (table 1). Both silver and gold correlate negatively with copper (fig. 38), a relationship that suggests that both precious metals are probably associated with galena or are not preferentially associated with any sulfide minerals. Care must be exercised in the interpretation of data from the Copper Chief, because much precious-metal-rich gossan ore was mined in preference to massive sulfide ore (Lindberg, written comm., 1990). Even considering this complication, lead and gold-rich, copper-poor massive sulfide deposits, although the norm in the Big Bug district, are present in other districts as well.

Production attributed to the Florentina Mine (also spelled "Florencia") during its lifetime includes metals produced by leaching high-grade copper ore from the United Verde Extension dumps. This mining practice may account for the apparently anomalously low silver and gold grades (0.009 oz/ton Ag and 0.0008 oz/ton Au) associated with Florentina ore. Data for the Green Monster and Galveston Mines possibly should be combined, because ore may have come from the same deposit. Metal ratios for the Galveston are highly skewed by 1936 data, having a Ag/Au of 500.

**ZONIA DISTRICT**

As mentioned in the overall district summary, data for the Zonia district, located southwest of Prescott (figs. 1, 39), are difficult to compare to data from other districts because open-pit mining of relatively low grade ore took place at the Zonia Mine during the 1960's and 1970's (Lundin, 1986). Because the Zonia Mine accounts for 99 percent of the tonnage from the district (table 10), pre-1960 data must be used to compare the Zonia district to other districts whose production was entirely from underground mines.

The Zonia deposit is localized within metarhyolite tuff, but very little massive sulfide ore is present (Anonymous, 1943; Kumke, 1947; DeWitt, 1983, 1987). Ore minerals are malachite, chrysocolla, minor galena, and minor cuprite. Pre-1960 production from the Zonia Mine consisted of copper-rich ore (2–10 percent) having unusually low silver grades (most less than 0.4 oz/ton) and moderate to slightly high gold grades (0.1–0.15 oz/ton). Silver and gold correlate well with each other for this period (fig. 40), but the resulting Ag/Au of 1–2 is anomalously low compared to the average for the state of 36. Lead, when produced, was between 0.03 and 0.20 percent. A block of about 400,000 tons of ore defined by diamond drilling and trenching (Kumke, 1947) averaged about 1.0–1.15 percent Cu, 0.2 oz/ton Ag, and 0.015 oz/ton Au. A much larger block of ore, perhaps an order of magnitude larger, averaged about 0.5 percent Cu. The Ag/Au of this larger block of ore was 13. These metal ratios are similar to those for some of the small deposits in the Agua Fria district, especially the Bigbug (also spelled "Big Bug"), Stoddard, and Yallar Kid Mines (table 1).
Figure 36. Plot of year of production vs. silver and gold in the United Verde Extension Mine, 1915–45. Symbols that plot on the x-axis indicate no data for silver or gold.

Figure 37. Plot of year of production vs. ore, copper, and silver in the United Verde Extension Mine, 1915–40.

Figure 38. Plot of copper vs. silver and gold in the Copper Chief Mine, 1901–48. Symbols that plot on the y-axis indicate no data for copper.
METAL ZONATION PATTERNS AND PROVINCES

Production data for the Zonia Mine from 1966 through 1974 are not particularly illuminating (fig. 41), because gold and silver were not recovered from the heap-leaching operations. Copper grade shows a reasonable correlation with tonnage mined, but copper concentrates having grades in excess of 80 percent Cu for 1971 and later years are obviously related to lifetime of the cyanide cycle for copper recovery and shutdown of the mine, not to mineralogic features. Significant amounts of precious metals could have been recovered from this oxidized ore, as suggested by metallurgical tests (Kumke, 1947).

METAL ZONATION PATTERNS AND PROVINCES

Base- and precious-metal concentrations in most Early Proterozoic massive sulfide deposits in Arizona are comparable to those in Archean massive sulfide deposits in Canada (Sangster, 1980; Franklin and others, 1981), in Cambrian deposits in Tasmania (Large and others, 1989), and in Tertiary massive sulfide deposits in Japan (Ishihara, 1974; Ohmoto and Skinner, 1983). Modern-day deposits along the mid-ocean-ridge systems have similar, but variable, base- and precious-metal concentrations (Hannington and Scott, 1989b). Although most deposits in Arizona cluster near the average of 3.6 percent Cu, 2–6 percent Zn, 1.3 oz/ton Ag, and 0.04 oz/ton Au, significant departures exist. Metal concentrations in the unusual deposits may reflect both first-order differences in tectonic setting of these deposits and second-order thermochemical conditions under which they were formed.

BASE–METAL CONCENTRATIONS

Most deposits in Arizona averaged between 2 and 6 percent Cu (fig. 42). Notably, however, deposits containing greater than 20,000 tons of ore in the Big Bug district averaged less than 2 percent Cu; the entire district averaged only 0.11 percent Cu. Of mines producing more than 20,000 tons of ore, only the United Verde Extension averaged greater than 4.4 percent Cu; its 10.2 percent Cu grade was largely a function of extreme supergene enrichment, which Lindberg (1986c, 1989) believed may be partly Tertiary in age. Such extreme enrichment is not representative of most deposits in the State. Importantly, low copper grades are not restricted to deposits in the Big Bug district, but are represented in the Old Dick district by the Copper King Mine (CK, fig. 42), in the Verde district by the Copper Chief (CC, fig. 42), Green Monster, and Galveston Mines, and in the Agua Fria district by the Pocahontas and Copper Dome Mines.

Variations in lead and zinc grades are more difficult to assess because of the sporadic nature of the production of those metals. When produced, zinc averaged 3–10 percent in the Agua Fria, Big Bug, Hualapai, Old Dick, and Verde districts. No zinc has been produced from the Kay, Mayer, New River, or Zonia districts. However, samples of pyritic ore from the Kay, Mayer, and New River districts contain minor, but visible sphalerite (Lindgren, 1926; Arizona Geological Survey, unpub. file data, 1984; DeWitt, unpub. data, 1988). Lead, when produced in seven of the nine districts (table 1), averaged between 0.02 and 1.8 percent. Notably, the Big Bug district had the highest grade (1.84 percent Pb) and a very low copper grade. Most of the other copper-poor deposits in the Old Dick, Agua Fria, and Verde districts also had elevated lead concentrations compared to the deposits having average copper grades.

PRECIOUS–METAL CONCENTRATIONS

The average gold and silver production grades of all deposits in Arizona were 0.037 oz/ton Au and 1.360 oz/ton Ag (table 1). Gold concentrations ranged from less than 0.001 oz/ton to 0.44 oz/ton (figs. 42 and 43); deposits producing more than 20,000 tons of ore ranged from less than 0.001 oz/ton Au to almost 0.12 oz/ton Au. Silver concentrations ranged from 0.009 oz/ton to 5.15 oz/ton; deposits producing more than 20,000 tons of ore
ranged from 0.009 oz/ton Au to 3.56 oz/ton Ag (fig. 43). Deposits having the highest overall gold and silver grades are concentrated in the Big Bug district (figs. 42 and 43), but include copper-poor deposits in the Agua Fria and Verde districts that contain elevated concentrations of lead, as discussed above. Deposits having anomalously low precious-metal grades are restricted, in large part, to the Old Dick and Hualapai districts (figs. 42 and 43.)

The Ag/Au for all deposits averages 37, but ranges from 1 to 462 (fig. 43). Deposits in the Old Dick and Hualapai districts and gold-poor deposits such as the Binghamton Mine, in the Agua Fria district (B, figs. 42, 43), and the Verde Central Mine, in the Verde district (VC, figs. 42, 43), have a Ag/Au greater than 100. These ratios are probably strongly affected by mining of small amounts of ore enriched in gold from small deposits that have a Ag/Au less than 10.

**FACTORS CONTROLLING ORE DEPOSITION**

Anomalously low copper grades (less than 1 percent Cu) and anomalously high lead grades (greater than 1 percent Pb) characterize the Big Bug district (figs. 42, 44) and set it apart from all other massive sulfide districts in Arizona. Importantly, deposits having the same characteristics as those in the Big Bug district (low copper, high lead) are also present in the Old Dick, Verde, and Agua Fria districts. Metavolcanic strata that host deposits in the Big Bug district are no different chemically (Anderson, 1989b; DeWitt, unpub. data, 1989) or by virtue of their age (Anderson and others, 1971; Karlstrom and others, 1987) or tectonic setting (Anderson, 1989b) from those in other districts in the Prescott-Jerome area. Therefore, processes responsible for
FACTORS CONTROLLING ORE DEPOSITION

the low copper and high lead grades must be related to local, not regional, conditions of ore deposition.

Very low silver and gold grades and a high Ag/Au characterize the westernmost two districts, Hualapai and Old Dick (figs. 43, 44). Deposits in these districts are hosted by thin metavolcanic sequences that are interbedded with (Hualapai) and over lain by (Old Dick) extensive metapelitic strata (Anderson and others, 1955; More, 1980; Stensrud and More, 1980; Wooden and DeWitt, 1991). These metavolcanic sequences may be 20 m.y. or more younger than those in the Prescott-Jerome area (Chamberlain and Bowring, 1990) and were probably formed in arcs or back-arcs immediately adjacent to or overlying Mojave-type continental crust (Wooden and DeWitt, 1991). Processes that caused the low gold and silver grades are probably controlled by major regional, not local, differences in the crust underlying western Arizona.

The Agua Fria district has abnormally low concentrations of precious metals, but has a Ag/Au similar to other districts in the Prescott-Jerome area. Deposits in this district that have low concentrations of precious metals are hosted within thick metahyloleite sequences (Anderson and Blacet, 1972b; Brook, 1974; O'Hara, 1986; Anderson, 1986b; DeWitt, 1987), not at the tops of such sequences, as are most deposits in the Prescott-Jerome area. The processes responsible for this precious-metal depletion are probably controlled by unique factors related to the depositional environment of massive sulfide deposits in the Agua Fria district.

CRUSTAL CONTROLS OF METALLOGENESIS

The existence of Mojave-type continental crust in the subsurface in western Arizona beneath the Hualapai and Old Dick districts at the time of volcanism and formation of the massive sulfide deposits (Wooden and DeWitt, 1991) is believed to be the first-order phenomenon that controlled the precious-metal-poor nature of deposits in these districts. Compared to central and southeastern Arizona, Early Proterozoic supracrustal rocks of the Mojave Desert region contain very few base- or precious-metal deposits that are of Early Proterozoic age (Fife and Brown, 1980; DeWitt, 1987). Therefore, Mojave-type continental crust in the subsurface of western Arizona may be impoverished in base and precious metals compared to Early Proterozoic volcanic strata characteristic of central Arizona. Because both metavolcanic strata and some of the younger pre- and post-tectonic plutons in western Arizona appear to have been derived, in large part from partial melting of Mojave-type continental crust (Wooden and DeWitt, 1991), those rocks and their associated massive sulfide deposits carry the characteristic signature of a high Ag/Au and low precious-metal concentrations.

This precious-metal-poor nature of the Early Proterozoic Mojave-type crust in the Mojave Desert region and western Arizona should not be confused with the gold-rich nature and the low Ag/Au characteristic of ~1,730-Ma and younger Proterozoic, and all Phanerzoic, vein deposits noted by Titley (1985, 1987, 1989) for his domain II, which corresponds to central and western Arizona. The southeastern boundary of Titley's (1987, 1989) domain II (high gold, low Ag/Au) is largely coincident with the southeastern boundary of 1,690- to 1,740-Ma pre-, syn-, and post-tectonic plutons (DeWitt, unpub. data, 1988; Anderson, 1989a) that increase in abundance to the northwest in Arizona and into the Mojave Desert, where they constitute 98 percent or more of the Early Proterozoic outcrops (DeWitt and others, 1984; DeWitt, 1987; Miller and Wooden, 1988; Wooden and others, 1988; Wooden and Miller, 1990). Titley's (1987, 1989) domain I is virtually lacking in these rocks and, instead, is characterized by the monotonous pelite and psammitic rock types of the Pinal Schist. The model suggested by this paper, and outlined by the data of Titley, is that the gold-rich nature and the low Ag/Au characteristic of domain II in central and western Arizona is a consequence of emplacement of enormous amounts of plutonic material from 1,690 to 1,740 Ma and recycling of precious metals from the plutonic material (and, to a lesser extent the pre-existing basement) throughout subsequent geologic time.

The depositional environment during formation of massive sulfide deposits is slightly different in the westernmost two districts as compared to all districts in central Arizona. In both the Hualapai and Old Dick districts, massive sulfide deposits are localized in relatively thin, laterally restricted volcanic piles that interfinger with or are overlain by pelitic metasedimentary rocks. This sediment-dominated tectonic environment may have had a second-order control on the concentration of precious metals in the deposits, but is not believed to be as significant as the first-order control discussed above. Also, most sediment-hosted massive sulfide deposits (Beshi-type deposits) do not, on average, have lower gold and silver concentrations than volcanogenic massive sulfide deposits (Franklin and others, 1981). Some Beshi-type deposits, such as Geco and Ducktown, do have lower concentrations of gold and silver (R.W. Hutchinson, written commun., 1993). Deposits having anomalously high gold and silver concentrations compared to the average for their districts are present in the Old Dick district; their significance is discussed next.

THERMOCHEMICAL CONTROLS OF METALLOGENESIS

Why does the Big Bug district contain much higher concentrations of gold, silver, and lead than other districts in the Prescott-Jerome area? Distal versus proximal volcanic setting of the deposits in the district has been suggested as a possible control of metallogenesis (Bouley and Hodder, 1976, 1977; Lindberg, 1989), but was rejected by Anderson
Figure 42. Plot of copper vs. gold for all massive sulfide deposits, Arizona. Large symbols indicate deposits that produced more than 20,000 tons of ore; small symbols indicate deposits that produced less than 20,000 tons of ore. Plus sign, deposits in Agua Fria district; open square, deposits in Big Bug district; open circle, deposits in Hualapai district; open triangle, deposits in Kay district; filled square, deposits in Mayer district; filled upside-down triangle, deposits in New River district; filled triangle, deposits in Old Dick district; filled circle, deposits in Verde district; cross, deposits in Zonia district; A, Antler Mine; B, Binghamton; BB, Bluebell; BR, Bruce, CC, Copper Chief; CK, Copper King; CW, Copper World; D, DeSoto; H, Hackberry; IK, Iron King; K, Kay; O, Orizaba (gold, when produced, was 0.02 oz/ton); OD, Old Dick; S, Stoddard; UV, United Verde; UVX, United Verde Extension; VC, Verde Central; Z, Zonia (pre-open pit mining; Z' is location of major ore blocked out by Kumke, 1947)

Figure 43. Plot of silver vs. gold for all massive sulfide deposits, Arizona. Large symbols indicate deposits that produced more than 20,000 tons of ore; small symbols indicate deposits that produced less than 20,000 tons of ore. Plus sign, deposits in Agua Fria district; open square, deposits in Big Bug district; open circle, deposits in Hualapai district; open triangle, deposits in Kay district; filled square, deposits in Mayer district; filled upside-down triangle, deposits in New River district; filled triangle, deposits in Old Dick district; filled circle, deposits in Verde district; cross, deposits in Zonia district; A, Antler Mine; B, Binghamton; BB, Bluebell; BR, Bruce, CC, Copper Chief; CK, Copper King; CW, Copper World; D, DeSoto; H, Hackberry; IK, Iron King; K, Kay; O, Orizaba (gold, when produced, was 0.02 oz/ton); OD, Old Dick; S, Stoddard; UV, United Verde; UVX, United Verde Extension; VC, Verde Central; Z, Zonia (pre-open pit mining; Z' is location of major ore blocked out by Kumke, 1947). Uppermost diagonal line is Ag/Au = 10; middle diagonal line is Ag/Au = 40; lowest diagonal line is Ag/Au = 100.
FACTORS CONTROLLING ORE DEPOSITION

Figure 44. Massive sulfide metallic mineral districts and metal zonation patterns in central and northwestern Arizona. Location of Pittsburgh-Tonto, Pranty’s Cabin, Gray’s Gulch, and Bronco Creek districts indicated, but district names are not shown. Numbers beneath district name are (top) Au (oz/ton) and (bottom) Ag (oz/ton); number to right of Au and Ag grades is Ag/Au; area in western Arizona underlain by Mojave-type crust shown by stipple pattern.

(1977) and is not favored by this author. Deposits suggested by Bouley and Hodder (1976) to be distal because of their metal ratios are, in fact, within thick accumulation of basaltic to rhyolitic flows. Therefore, the deposits were not formed in distal volcanic settings. Deposits, however, may have been distal or proximal with regard to localized feeder zones and hydrothermal centers. Thermochemical controls of ore deposition (Eldridge and others, 1983; Huston and Large, 1989; Large and others, 1989), and specifically, temperature and sulfur fugacity of hydrothermal solutions responsible for ore deposition (Hannington and Scott, 1989a) may have been the principal factor for the differences in metal concentrations and ratios. From their study of Archean through modern volcanogenic massive sulfide deposits from various submarine tectonic environments, Hannington and Scott (1989a) presented both theoretical and empirical evidence for precious-metal enrichment in low-temperature (<300°C), sulfur-rich deposits characterized by lack of pyrrhotite and low iron content of coexisting sphalerite.

Much of the data from Arizona deposits supports this model. Pyrrhotite is lacking at the Iron King Mine in the Big Bug district. An analysis of brown sphalerite, which accounts for more than 90 percent of the sphalerite in the deposit, contained 3.2 percent Fe, which amounts to 5.5 mole percent FeS (Anderson and Creasey, 1958, p. 167). Iron concentrations of sphalerite that are this low are associated with gold grades of about 2–5 ppm for selected Archean massive sulfide deposits in eastern Canada (Hannington and Scott, 1989a, table 1). Analytical data are lacking for the temperature of deposition of ore minerals in the Big Bug district, but the above observations suggest that the gold-, silver-, and possibly lead-rich nature of the ore in this district is a function of low temperature (<300°C and possibly as low as 250°C) deposition of gold- and silver-rich brines in a sulfur-rich, proximal volcanic setting. By comparison, pyrrhotite is a typical ore mineral at the Antler Mine, in the Hualapai district, and the Old Dick Mine in the Old Dick district. Sphalerite is rich in iron in both deposits, and gold grades at the two deposits are among the lowest in the State.

Therefore, the model that is favored to explain those deposits that were previously interpreted to have formed in a distal volcanic setting is one that has low-temperature hydrothermal fluids depositing gold-, silver-, and possibly lead-rich minerals in a proximal volcanic setting. The presence of Big Bug-like deposits in the Old Dick, Verde, and Agua Fria districts (figs. 42 and 43) is further evidence that
distal volcanic setting is not the cause of these apparently anomalous metal ratios and concentrations. The Copper King deposit, in the Old Dick district, is within metabasalt flows of the Bridle Formation and is as proximal as other massive sulfide deposits in the district (Anderson and others, 1955; Conway and others, 1986b), but it is rich in gold, silver, and lead compared to surrounding deposits. The Copper Chief, Green Monster, and Galveston deposits in the Verde district (fig. 32), are localized at the upper contact of thick metabasalt sequences that have minor metarhyolite components, but have anomalously low copper, gold, and silver concentrations. Similarly, the Pocahontas and Copper Dome deposits, in the Agua Fria district, are in settings that are as proximal as other massive sulfide deposits in the district, but have the characteristic metal ratios of the Big Bug district. Individual deposits within the proximal volcanic terrane, however, may have been distal to local vents.

Remaining to be explained are the anomalously precious-metal-poor deposits of the Agua Fria and Verde districts (figs. 42 and 43) that have otherwise normal base-metal concentrations. The Verde Central and Cleopatra deposits in the Verde district and the Binghamton deposit in the Agua Fria district are hosted within thick metarhyolite units, not at the contacts of metarhyolite with more mafic rocks. As one possibility, deposits of this type may be related to high-temperature (>350°C) hydrothermal fluids that were not capable of transporting and depositing precious metals in elevated concentrations. Such deposits may have been short-lived hydrothermal systems developed within actively erupting riftic complexes (Lindberg, 1986c; DeWitt, 1987; O'Hara, 1987b).

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