Geologic Settings of Wulfenite in Arizona

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March 21, 2009

Arizona is famous for its spectacular wulfenite specimens. The butterscotch-colored, bladed crystals from the Glove Mine in the Santa Rita Mountains south of Tucson and the bright red, chunky blades from the Red Cloud Mine in the Silver district north of Yuma are prized highlights of many mineral collections. Most of these famous mineral localities are no longer available to collectors, making the historic specimens even more valuable.

Outline

- Alkali-calcic Pb-Zn-Ag
  - Laramide (75-65 Ma)
    - Glove, Tyndall, Turquoise, Empire dist.
  - Mid-Tertiary (30-20 Ma)
    - Hilltop, Tonopah, Hull, Red Cloud (Silver dist.), Ripsey, Grand Reef, Purple Passion mines
- Quartz Alkalic Au-base metal
  - Jurassic (180-160 Ma)
    - Bisbee
  - Laramide (75-70 Ma)
    - Old Yuma
  - Mid-Tertiary (28-22 Ma)
    - Tiger, Rowley
- Calc-alkalic porphyry copper stage 4
  - Laramide (68-54 Ma)
    - 79, Chilito, Christmas, Finch, Troy
- Peraluminous Calcic (Au-base metals)
  - Precambrian (~1700 Ma)
    - Cave Creek, Hieroglyphic Mts.
  - Jurassic (~175-150 Ma)
    - Western Arizona deposits
  - Late Laramide (60-45 Ma)
    - Vulture mine
- Peraluminous Calc-alkalic (W-base metals)
  - Precambrian?
    - Tungstona, Picacho View mines
  - Jurassic? (175-160 Ma)
    - Mildren (Cababi district) mine
  - Late Laramide (60-45 Ma)
    - Campo Bonito district, Three Musketeers

Figure 1. Wulfenite from the Glove mine, Santa Rita Mountains

Wulfenite is lead molybdate, $PbMoO_4$. It forms in the oxidized zones of lead deposits where the white needle-like crystals of cerussite ($PbCO_3$) have developed. Surprisingly, the presence of molybdenite is not required. Wulfenite rarely occurs in the same mineral deposits as molybdenite, and then only in the later stages of the deposits. Even there, wulfenite does not occur unless cerussite or mimetite is present. There had to be enough lead in the system in a relatively soluble mineral to allow the molybdenum in the ground water to combine with lead and oxygen as wulfenite.

Most specimens photographed for this article are on display at the Arizona Mining and Mineral Museum. For explanations of the terms used in this article, see articles by Jan C. Wilt that are reproduced on Jan's website at www.janrasmussen.com. Click on Current Research, then on the appropriate article.

ALKALI-CALCIC PB-ZN-AG DISTRICTS

Some of the most stunning collectable specimens of wulfenite occur in lead-zinc-silver districts. These mining districts are associated with igneous rocks whose whole rock chemistry plots in the alkali-calcic field in a diagram of

%K_2O versus %SiO_2. These types of igneous rocks produced hydrothermal fluids that contained lead, zinc, and silver in solution in the hot water. Other metals were sequestered in the mineral structures of the rock-forming minerals. The Pb-Zn-Ag-rich hydrothermal fluids then intruded into veins, stockworks, and fractures, and in some cases replaced limestone formations in the host rocks.

The alkali-calcic districts that contain the most abundant and best specimens of wulfenite were deposited during two time periods: the early Laramide (75-65 million years ago [Ma]) and the mid-Tertiary (25-15 Ma).

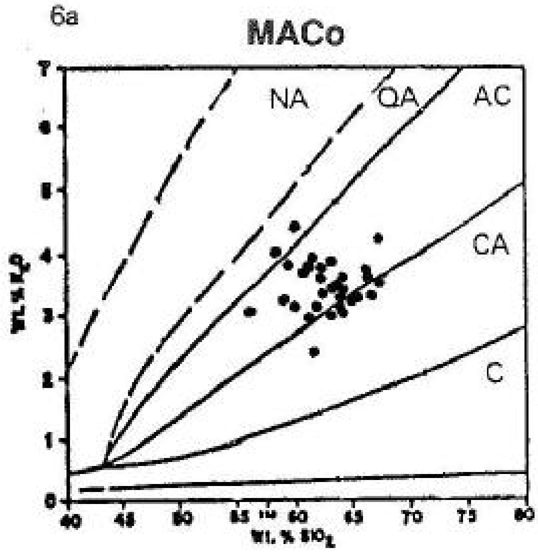

Figure 2. Alkali-calcic, oxidized plutons: whole rock chemistry of igneous rocks associated with lead-zinc-silver deposits (Wilt, 1995)

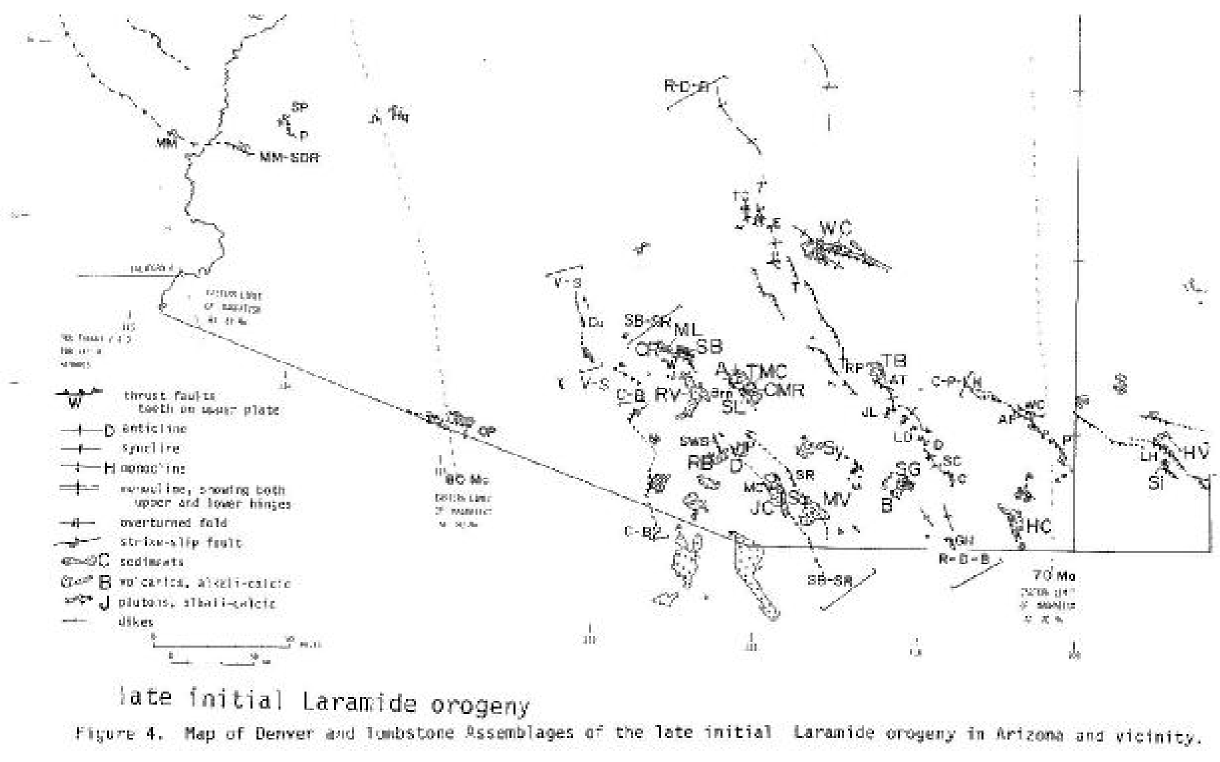

Figure 3. Igneous and sedimentary rocks and structures associated with lead-zinc-silver deposits of Laramide age (from Keith and Wilt, 1986)

Lead-Zinc-Silver Mining Districts of Laramide Age (~75-65 Million Years Ago)

Examples of the alkali-calcic mining districts of early middle Laramide age that contain wulfenite include: the Glove mine in the Tyndall district in the northwestern Santa Rita Mountains, the Emerald-Silver Plume and Toughnut mines in the Tombstone area, the Silver Bill, Defiance, Mystery, and Tom Scott mines in the Turquoise district (Courtland-Gleeson area), and the Total Wreck, Gopher, Prince (Hilton) mines in the Empire Mountains. Other examples, such as the Hardshell and Hermosa mines (Harshaw district), Pomona mine (Vekol district), and Sunset mine (Pajarito district) are listed in Wilt and others (1984).

The wulfenite at the Glove Mine occurs with argentiferous galena, sphalerite, with small amounts of pyrite, chalcopyrite and quartz. The minerals were deposited in permeable zones at the intersection of a bedding plane fault and favorable beds in the Permian Naco Limestone. There was extensive solution of the limestone and the deep oxidation concentrated cerussite, anglesite, wulfenite, and smithsonite in the leached caverns as sand carbonate ore. There were shaft and adit operations, as the mine was worked at various times between 1911 and 1972. The Glove mine produced 29,260 tons of ore averaging about 22% lead, 9% zinc, 0.3% copper, and 7 oz silver per ton, with minor gold (Keith, 1975; Wilt and others, 1984).

Figure 4. Glove mine wulfenite

The Turquoise district in the Courtland Gleeson area of southeastern Arizona produced excellent wulfenite specimens from several mines, such as the Defiance, Mystery, and Silver Bill mines. The Silver Bill mine was a lead-zinc-silver mine that contained irregular small stringers, pockets, and replacement bodies of oxidized base metal sulfides in Pennsylvanian-Permian Naco Group Limestones that is in contact with a Laramide quartz monzonite porphyry. There were large tonnages mined from shaft workings connected to the Mystery mine during the 1800s. In addition, 6,570 tons of ore were produced during 1922-30 and 1938-41 (Keith, 1973).

Figure 5. Wulfenite from the Silver Bill Mine, Turquoise district

The Defiance mine, which is also in the Turquoise district, contains large amounts of magnificent wulfenite specimens that line solution cavities and that occur in oxidized lead, manganese, and iron deposits. The wulfenite is associated with cerussite, anglesite, malachite, smithsonite, cerargyrite, and pyrolusite. The lead-zinc-silver orebodies are in Pennsylvanian-Permian Naco Group limestones. They occur where fractures intersect or change dip or they are parallel to bedding. They are associated with aplite dikes related to the Sugarloaf Quartz Latite Porphyry of possible Cretaceous (75 Ma) or Jurassic age (Keith, 1973; Wilt and others, 1984).

Figure 6. Wulfenite from Defiance mine donated by Lorraine Kilpatrick

Wulfenite has also been reported from the Total Wreck Mine in the Empire Mountains southeast of Tucson. The wulfenite is associated with cerussite, vanadinite, cerargyrite, malachite, azurite, chrysocolla and minor copper and lead sulfides. The ore occurs in irregular replacement orebodies in badly faulted Permian limestone beds intruded by Laramide diorite stringers and dikes. There are shafts and tunnels that were worked from the 1880s to 1940. These produced about 14,000 tons of ore averaging 8% lead, 6 oz silver per ton, and minor gold and copper. Eight tons of molybdenum concentrates were produced for the war effort in 1918 (Keith, 1974; Wilt and others, 1984).

Lead-Zinc-Silver Mining Districts of mid-Tertiary Age (~30-20 Million Years Ago)

Wonderful wulfenite specimens also come from lead-zinc-silver mining districts of mid-Tertiary age. These include the bright red specimens from the Red Cloud mine, and some from the Aravaipa district in the Galiuro Mountains and the Hilltop mine in the Chiricahua Mountains.

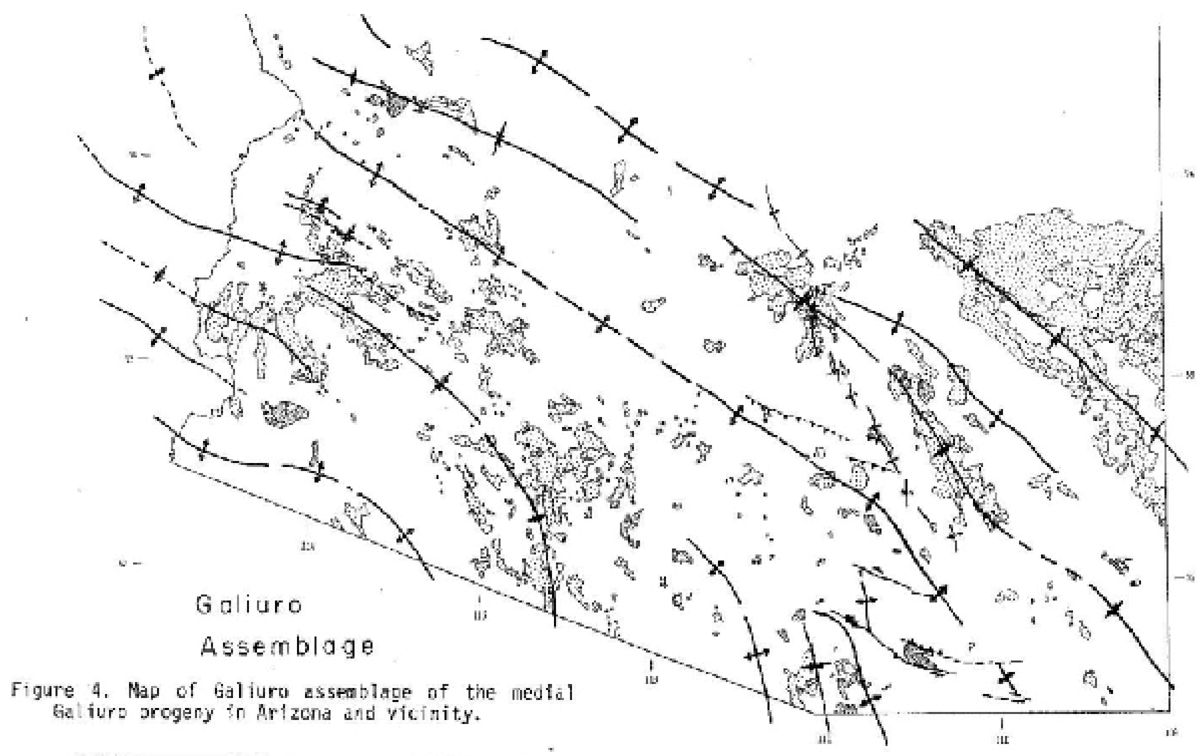

Figure 7. Outcrops of igneous rocks related to mid-Tertiary lead-zinc-silver districts (from Keith and Wilt, 1985)

The Red Cloud Mine in the Silver mining district of Yuma County is most famous for its barrel-shaped, bright red vanadinite crystals. But it also contains unusually bright red wulfenite crystals that have a slightly more chunky shape than the usual blades. The minerals occur in irregular masses and vug linings of argentiferous lead and zinc carbonates with pyrolusite, vanadinite, wulfenite, and minor malachite. Nodules of partly altered argentiferous galena, and disseminated masses of silver chloride and bromide occur in a gangue of iron oxides, quartz, fluorite, calcite, gouge, and brecciated wall rock. The mineralized vein occurs in an irregular fault zone between Tertiary andesite breccia, dacite porphyry, rhyolite to dacitic tuffs and lapilli tuffs that intrude Laramide granodiorite to quartz diorite. The ore had an average grade of 5-6% lead and 10 oz silver per ton. The shaft operations in the 1880s produced a total (until the 1960s) of 21,000 tons of ore averaging 18 oz silver per ton and 5.5% lead and minor gold (Keith, 1978; Wilt and others, 1984).

Figure 8. Wulfenite from the Red Cloud mine donated by Les and Paula Presmyk

Specimens of wulfenite from the Hilltop mine in the California district of the Chiricahua Mountains in Cochise County are the more typical butterscotch yellow color. The wulfenite occurs with galena, cerussite, sphalerite, and spotty copper oxides and scheelite. The ore occupies fissure veins and irregular replacement lenses and bodies in banded and tilted, silicified Mississippian to Permian limestones and quartzites. Extensive workings from several tunnels produced a total of 30,000 tons of base metal sulfide ore intermittently from the early 1910s to 1954 (Keith, 1973; Wilt and others, 1984).

Figure 9. Wulfenite from the Hilltop mine in Cochise County

Another possible mid-Tertiary mine with unusual acicular wulfenite crystals and epitaxial needle growth over tabular crystals is the Purple Passion mine in the White Picacho district, also called the Diamond Joe mine, which is near the Great Southern mine. It occurs with fluorite, calcite, galena, anglesite, cerussite, chlorargyrite, smithsonite, willemite, and quartz. In the mid 1920s, about 60 tons of ore per week were being processed for a short time, averaging 12-15% lead, 13.5 oz Ag/ton, and minor gold.

Figure 10. Wulfenite from the Purple Passion mine in Yavapai County (Photos and data from www.fluorescents.com/mr2001.htm).

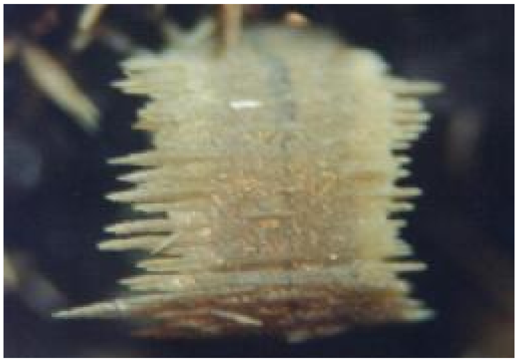

Figure 11. Epitaxial needle growth over tabular crystals of wulfenite, Purple Passion mine, Yavapai County (www.fluorescents.com/mr2001.htm).

QUARTZ ALKALIC GOLD-BASE METAL DISTRICTS

Wulfenite from mining districts associated with quartz alkalic igneous rocks occurs in the lead-zinc-silver zones with mineralization from three different time periods in Arizona: Jurassic, Laramide, and mid-Tertiary.

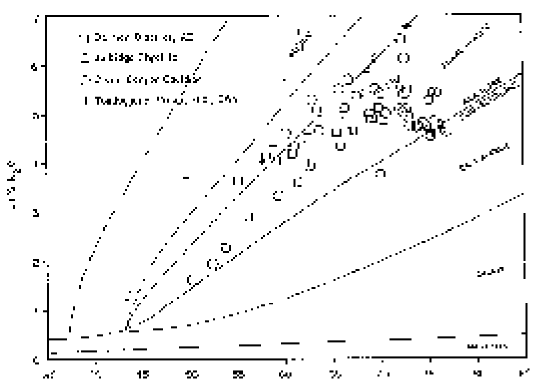

Figure 12. Quartz alkalic, oxidized plutons: whole rock chemistry of igneous rocks associated with gold-base metal (modified from Keith and others, 2005)

Gold-Base Metal Mining Districts of Jurassic Age (~180 Million Years Ago)

Minor occurrences of wulfenite occur in the Campbell orebody at Bisbee in the Warren mining district related to the Jurassic age (186-163 Ma) Juniper Flat Granite. The Campbell orebody contained oxidized base metals (malachite, azurite, cerussite, smithsonite, mimetite, and wulfenite) on the 1,700 - 2500 level. The minerals were in replacement bodies in lower Paleozoic limestones related to Jurassic porphyry dikes and sills. The shaft workings probably produced several hundred thousand tons of ore (Keith, 1973; Wilt and others, 1984).

Gold-Base Metal Mining Districts of Laramide Age (~75 Million Years Ago)

The Old Yuma mine in the northern Tucson Mountains was primarily a gold mine, previously owned by Richard Bideaux. The mineralization consists of partly oxidized base-metal sulfides with spotty wulfenite and vanadinite, and gangue quartz and calcite. The minerals occurred as a steeply dipping, lensing and faulted orebody along a fracture zone cutting Cretaceous volcanics and associated with a Laramide porphyry intrusive, the Amole Granite. Shaft and underground workings produced ore from 1916-1947, totaling 5,700 tons ore grading 4% lead, 1% copper, 0.6% zinc, 0.3% molybdenum, 1 ounce silver per ton, and 0.1 ounces gold per ton (Keith, 1974; Wilt and others, 1984). The mine is now in Saguaro National Park and is unavailable for collecting.

Figure 13. Wulfenite from the Old Yuma mine, Tucson Mountains

Gold-Base Metal Mining Districts of mid-Tertiary Age (~25-15 Million Years Ago)

Some of the most sought after wulfenite are the specimens from the Mammoth-St. Anthony Mine near the Tiger town site. This mine was on the land position of BHP Billiton's now closed San Manuel mine and the ore was used in the plant as flux in the copper smelting process.

Figure 14. Wulfenite from the Mammoth-St. Anthony mine

The wulfenite occurs with vanadinite, gold in quartz, galena, sphalerite, anglesite, cerussite, and many oxidized minerals. The ore occurs in west-northwest trending shear zones that are intruded by mid-Tertiary (22 Ma) rhyolite. The widest fissure veins occur in Precambrian quartz monzonite (Oracle Granite), which is the most intensely shattered and brecciated host in the mine area. The deposit was oxidized and faulted, and the thin wulfenite and vanadinite mineralization was deposited during the later period of oxidation. About 6.3 million pounds of molybdenum concentrates (MoO_3) were produced between 1881-1947 (Wilt and others, 1984).

Figure 15. Wulfenite from the Mammoth-St. Anthony mine on loan from the Arizona Mineral and Mining Museum Foundation (AMMMF)

The shafts and adits of the Mammoth-St. Anthony mine were closed in 2005 as part of the closure of the San Manuel mine and are no longer available for collecting. The San Manuel deposit was emplaced during the Laramide, which is typical of most other porphyry copper deposits in Arizona.

The Rowley mine in the Painted Rock district of Maricopa County is also a favorite for mineral collectors. Wulfenite occurs with barite, cerussite, and base-metal sulfides, especially with secondary minerals of a cerussite-anglesite suite, a wulfenite suite, a caledonite suite, and a vanadinite suite. The minerals occur in northwest trending fissure veins in mid-Tertiary andesite and rhyolite flows and dikes. The mine shipped 130 tons of wulfenite concentrate to California (grading 18.26 % MoO_3).

Figure 16. Wulfenite from the Rowley mine, Maricopa County, donated by Floyd and Alice Getsinger

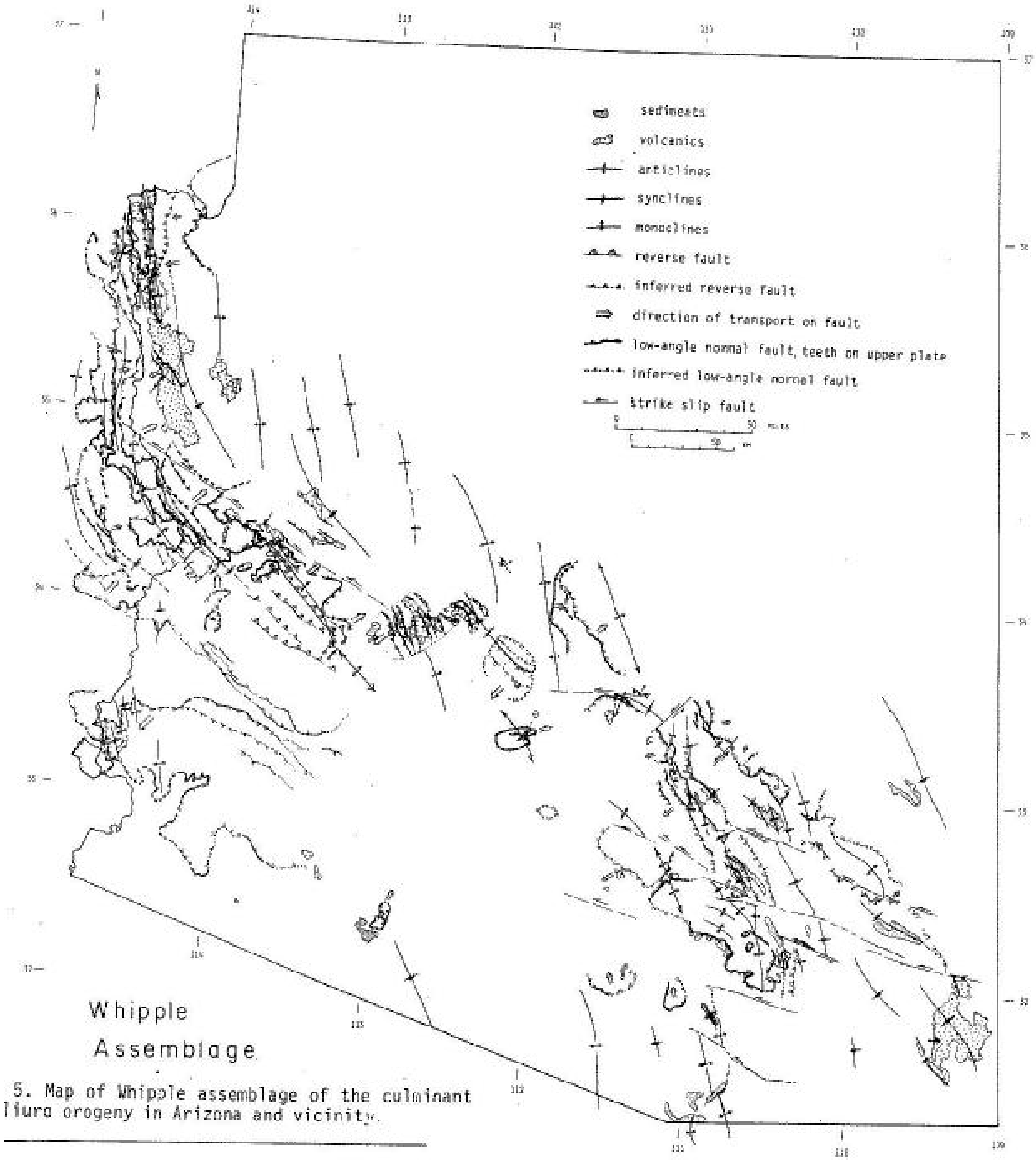

Figure 17. Igneous and sedimentary rocks and structures possibly related to mid-Tertiary gold districts (from Keith and Wilt, 1985)

CALC-ALKALIC PORPHYRY COPPER DEPOSITS

Stage 4 of Porphyry Copper Deposits of Laramide Age (~75-55 Ma)

Minor occurrences of wulfenite have been reported from the Stage 4 zones (later) of porphyry copper mining districts that are associated with igneous rocks of calc-alkalic whole rock chemistry. These Stage 4 deposits are characterized by quartz stockworks and veins associated with quartz-feldspar porphyrys and associated molybdenum-quartz-sericite-pyrite mineralization and minor arsenic (mimetite). Examples of Stage 4 zones in porphyry copper districts reporting wulfenite include the Chilito, Christmas, and 79 mines.

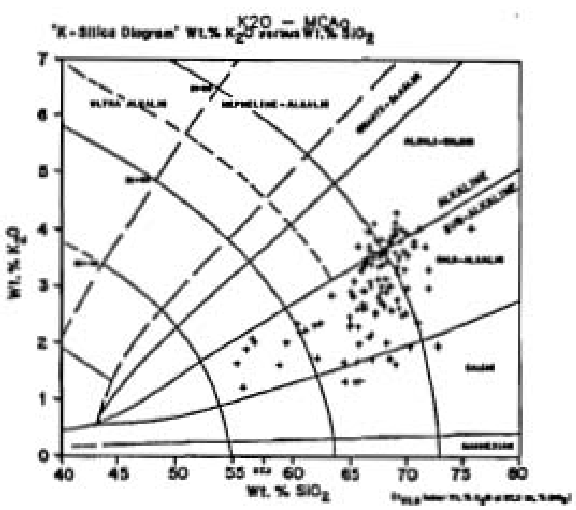

Figure 18. Calc-alkalic, oxidized plutons: whole rock chemistry of igneous rocks associated with porphyry copper deposits (Wilt, 1995)

At the 79 mine near the Ray mine, wulfenite occurs with galena, sphalerite, pyrite, and cerussite, along with a large variety of secondary minerals. The mineralization occurs in permeable zones, such as breccias, fractures, and shear zones, especially as bedded and vein replacements. The mineralization is usually in favorable rock types, such as contact metamorphosed Pennsylvanian Naco Limestone and silicified rhyolite porphyry dikes of probable Laramide age (62 Ma).

Figure 19. Wulfenite from the 79 mine (photo by John Callahan, not in the museum collection)

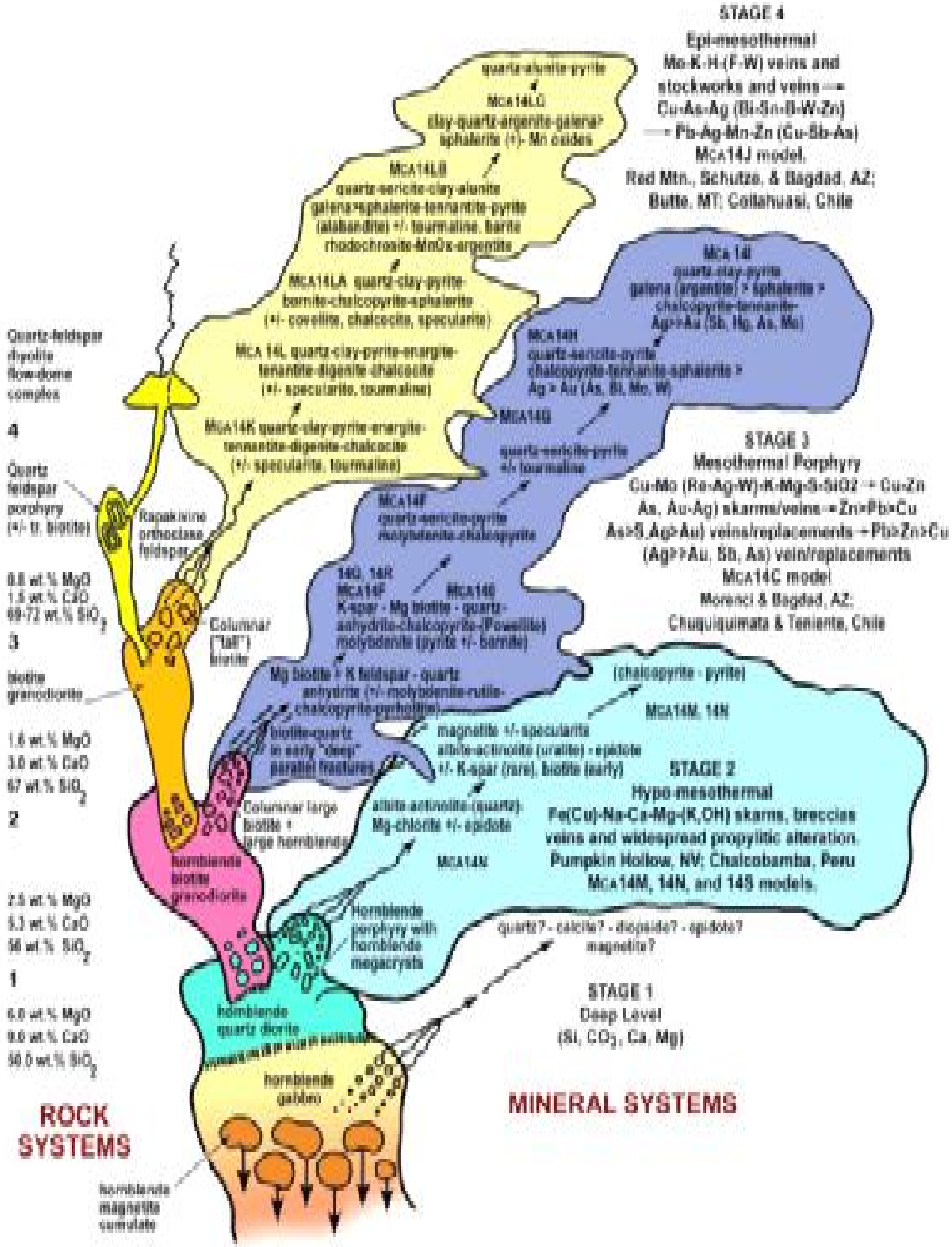

Figure 20. Stages of fluid release and differentiation products of calc-alkalic, oxidized plutons (Keith)

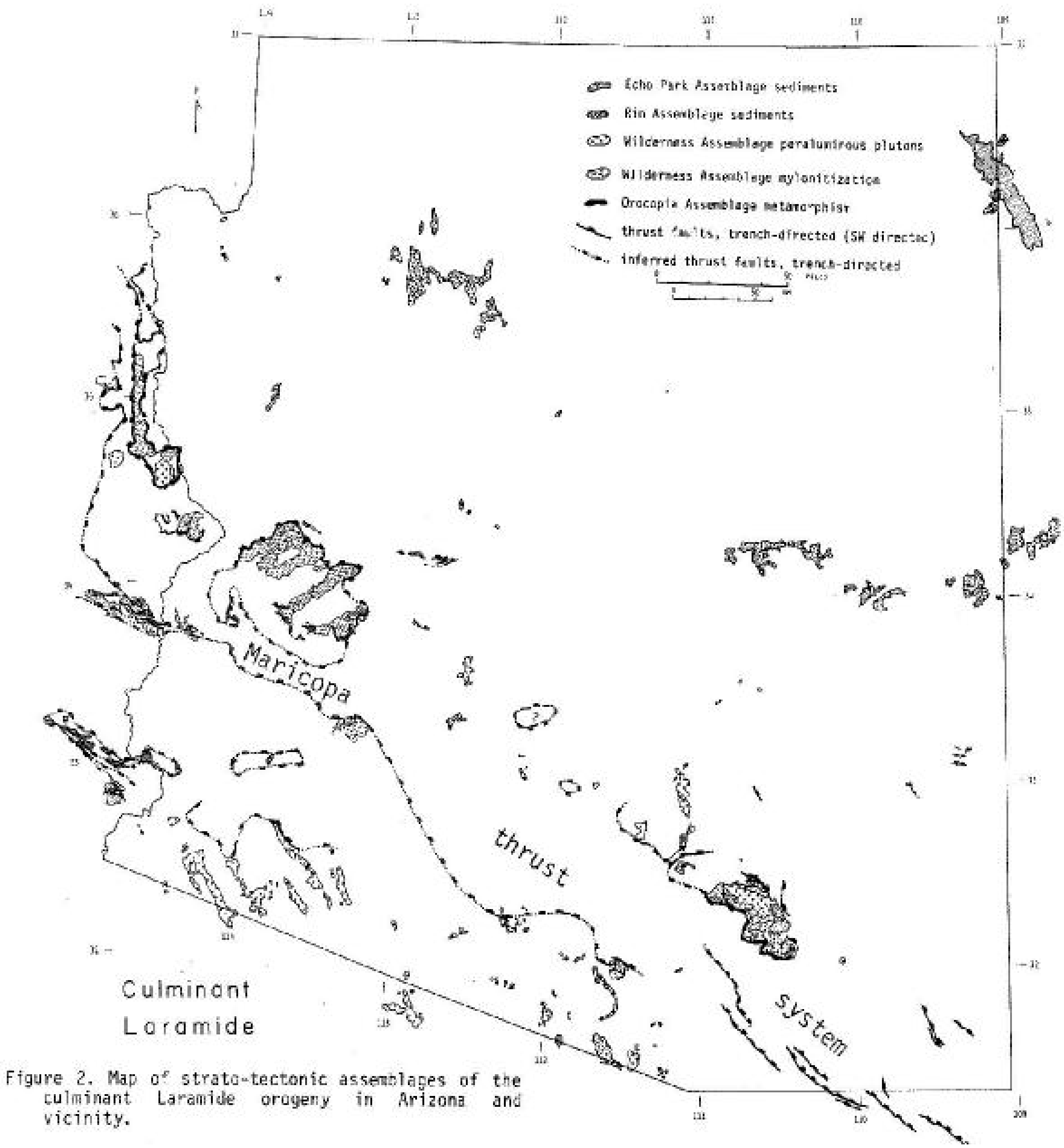

Figure 21. Outcrops of igneous and time-equivalent sedimentary rocks of the late Laramide peraluminous gold or tungsten districts (from Keith and Wilt, 1985)

PERALUMINOUS

Peraluminous plutonic rocks are commonly termed two-mica granites or "S" granites emplaced during flat subduction in Cordilleran plate tectonic settings. Wulfenite occurs in deposits associated with two types of alkalinity: calcic (gold-base metal related deposits) and calc-alkalic (tungsten-base metal related deposits). One of the better plots to distinguish between the two types of plutons is the rubidium vs. strontium variation diagram (Figure 22).

Peraluminous plutons have been emplaced in Arizona during several time periods: Precambrian, Jurassic, and Laramide.

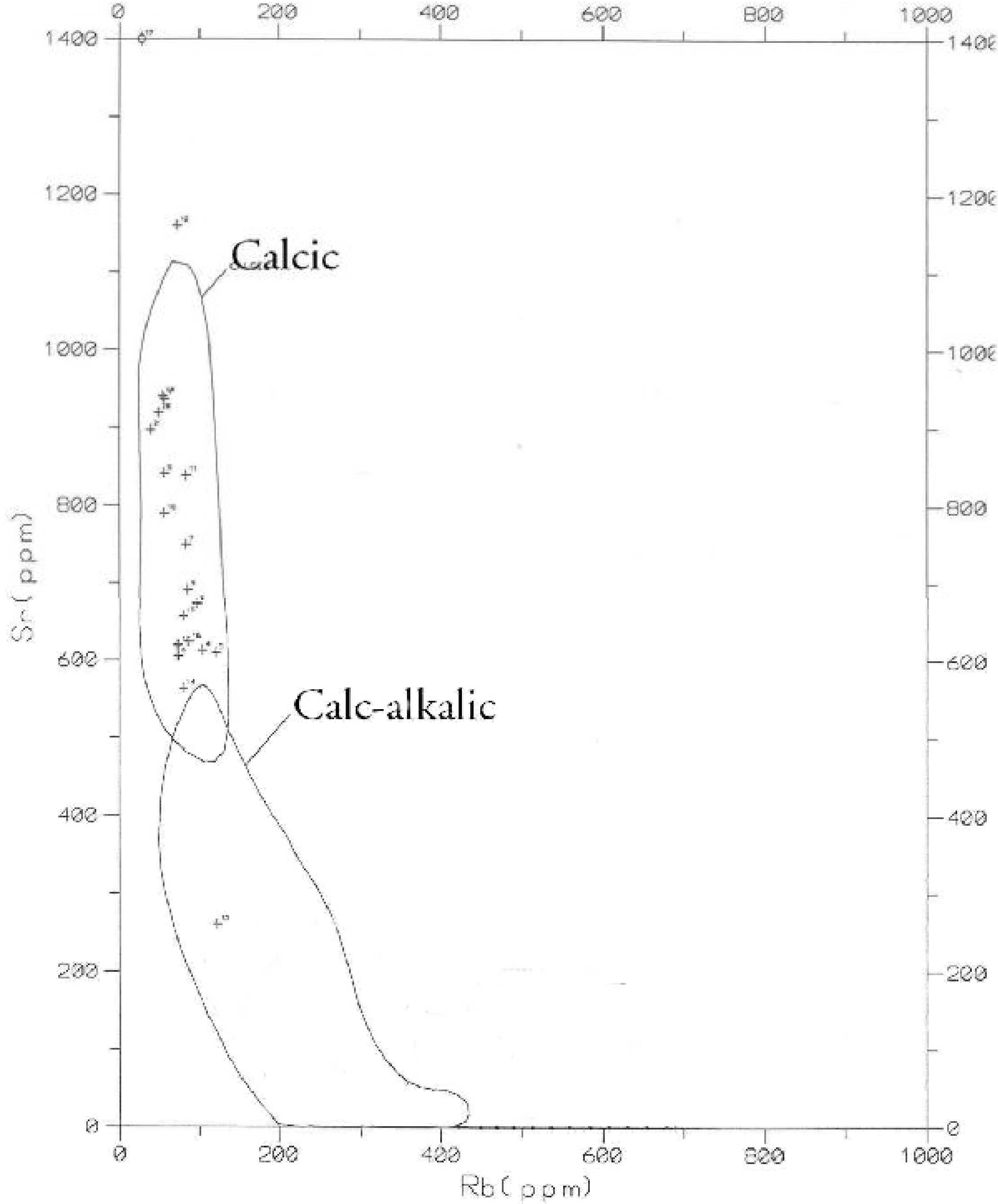

Figure 22. Rubidium vs. strontium plot showing fields of peraluminous calcic and calc-alkalic, oxidized plutons indicating whole rock chemistry of igneous rocks associated with gold (calcic) or tungsten (calc-alkalic) deposits (Keith and others, 1995)

PERALUMINOUS CALCIC AU DEPOSITS

Precambrian? (~1700 Ma) Gold-Base Metal Deposits

Although age dates and whole rock chemistry from the associated stocks are uncertain, it is possible that the Maricopa mine in the Cave Creek district, Prince of Arizona mine in the Hieroglyphic Mountains, and Lucky Strike claim in the White Picacho districts are Precambrian. These mines are hosted in Yavapai Schist and contain gold with oxidized lead minerals in fissure veins in fault zones

Jurassic (~175-150 Ma) Gold Deposits

There are numerous potential candidates for peraluminous calcic deposits of gold-base metal systems in western Arizona. However, age date and whole rock chemistry on such systems is currently lacking. Some of the systems that have been interpreted as mid-Tertiary detachment deposits may have been deposited during the Jurassic (Keith, 2007, SME talk).

Late Laramide (60-45 Ma) Gold Deposits

The culminant stage of the Laramide orogeny experienced flat subduction, which produced two mica granites throughout southern Arizona. Possible representatives of this type are the Kofa and Vulture mines. Characteristics of peraluminous calcic gold-base metal deposits include veins and stockworks or disseminations and breccias. They contain gold, lead, and some arsenic, tellurium, and bismuth. These deposits contain wulfenite and mimetite in the oxidized zones. Another example of this type of deposit is the San Francisco mine in Mexico.

PERALUMINOUS CALC-ALKALIC BASE METAL-TUNGSTEN DEPOSITS

Late stage pegmatite deposits containing boron, lithium, beryllium and minor tantalum, niobium, cesium, bismuth copper, uranium, fluorine, tungsten, tin, and phosphorous are typical of peraluminous calc-alkalic stocks and dikes related to low-angle subduction zones. This type of pluton is related to tungsten deposits and other rare minerals. They were intruded throughout Arizona during three time periods: Precambrian, Jurassic, and late Laramide.

Precambrian? Pegmatites or Tungsten Mines

Possible peraluminous calc-alkalic stocks and pegmatites of Precambrian age include those related to the Tungstona mine of the Eureka district of Yavapai County, and the Outpost and Picacho View mines of the White Picacho district. Wulfenite is only a minor occurrence in these districts.

Jurassic Tungsten Deposits (175-160 Ma)

The Mildren and nearby mines in the Cababi district of Pima County contain abundant wulfenite associated with vanadinite, cerussite, mimetite, and chrysocolla in brecciated quartz fissure veins in Jurassic amygdaloidal andesite flows.

Late Laramide Tungsten Deposits (60-45 Ma)

Possible peraluminous calc-alkalic districts include the Three Musketeers mine, and the Bear Cat claim of the Campo Bonito (Old Hat) district near Tucson, which may be related to the Wilderness granite suite of stocks and dikes of Laramide age. This district contains tungsten as scheelite and minor wulfenite and vanadinite and pyrite in north-northeast quartz veins in Precambrian granite near Laramide dikes. Without age dates and whole rock geochemistry, these assignments are speculative.

CONCLUSIONS

Minerals associated with wulfenite always include cerussite, and sometimes include vanadinite or mimetite. As the preceding descriptions of the individual mines indicate, wulfenite primarily occurs in the presence of the lead carbonate, cerussite. Most of the above wulfenite localities are in lead-zinc-silver mining districts or in the lead-rich zones of other types of deposits. Galena has been oxidized to cerussite by circulating ground water, which may be the most likely source of the molybdenum in the molybdate. None of the mines with good wulfenite specimens contained the molybdenum sulfide, molybdenite (MoS_2).

The best guide to good wulfenite localities is the presence of cerussite in lead-zinc-silver mining districts. A relatively complete description of the occurrences of molybdenum in Arizona is listed in Wilt and others, 1984).

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