rhenium resources in Arizona, there appear to be a few hundred tons of this metal that are associated with the molybdenum resources. The production of rhenium may be expected to increase considerably.

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**NIOBium AND TANtaLUM**

(By R. L. Parker, U.S. Geological Survey, Denver, Colo.)

**INTRODUCTION**

Niobium (columbium) and tantalum are rare metals that have become increasingly important in modern technology; they are used in certain electronic, nuclear, chemical, and high temperature metallurgical applications. Both metals are used for vacuum tube elements, superconductors, and corrosion-resistant equipment and laboratory ware, and as constituents in high temperature nonferrous alloys. These metals, in the form of ferrocolumbium or ferrotantalum-columbium, are used in the manufacture of special types of steel. Niobium and tantalum carbides are used in hot-forging dies, cutting tools, and jet engine turbine blades. Niobium especially is used for cladding and alloying nuclear fuels, whereas tantalum is used for capacitors, rectifiers, and surgical implants (Miller, 1959; Barton, 1962; Stevens, 1965a, b).

Various substitutes for columbium are vanadium in stainless steel; molybdenum, vanadium, tungsten, and ceramic coatings in high temperature applications; and alloys of technetium, vanadium, tin, and gadolinium in certain applications in the control of nuclear fusion reactions. Substitutes for tantalum include aluminum, silicon, germanium, selenium, zirconium, titanium, and misch metal in various electronic applications; and platinum, niobium, and zirconium in corrosion-resistant materials.

The United States is the world's largest consumer of niobium and tantalum, relying almost entirely on foreign sources, principally Nigeria, Congo, Brazil, and Canada for its ore supply. Critical shortages of these metals, caused by expanded wartime use, resulted in government allocation controls during World War II and the Korean conflict. During 1952-55 domestic and foreign ores were purchased at bonus prices by the government for stockpiling purposes. The program was extended to 1958 for domestic ores.

The U.S. annual imports and production and world annual production are shown in figure 35. During the last 14 years, imports of niobium-tantalum concentrates have ranged from an all-time high of 11,590,528 pounds in 1955 (reflecting government stockpile purchasing) to a low of 3,591,530 pounds in 1958. Imports have generally increased each year since 1958 to the 1966 level of 11,421,000 pounds.
Niobium and tantalum do not occur in nature as free metals, but are found commonly together as constituents of minerals that are compounds of niobium, tantalum, and oxygen with subordinate amounts of titanium, iron, manganese, rare earths, uranium, thorium, and other metals. Important ore minerals are columbite-tantalite \((Fe,Mn)\text{Nb}_2\text{O}_5\); pyrochlore \(NaCa\text{Nb}_2\text{O}_6\text{F}\); yttrotantalite \((Fe, Y, U)\text{Nb}_2\text{O}_5\); microlite \((Na,Ca)_2\text{Ta}_2\text{O}_5\text{(OH,F)}\); euxenite \((Y,\text{Ca,Ce,U, Th})\text{Nb}_2\text{O}_6\); fergusonite \((Y,\text{Ca,U, Th})\text{Nb}_2\text{O}_5\); and samarskite \((Fe,Y,U)\text{Nb}_2\text{Ti}_2\text{O}_9\). Niobium and tantalum are also contained in various amounts in titanium minerals—sphene, rutile (ilmenorutile), and ilmenite (Palache and others, 1944).

Contrary to general opinion, niobium is a fairly common element in the earth’s crust; it is about as abundant as cobalt and more plentiful than lead. Tantalum is much scarcer than niobium but more abundant than antimony, silver, or gold. However, compared with many other valuable elements whose crustal abundances are less than niobium or tantalum and which tend to concentrate in discrete ore bodies, concentrated deposits of niobium and particularly tantalum are scarce.

Niobium and tantalum minerals are found in certain granitic rocks and pegmatites, alkaline rock complexes and carbonatites, and placers derived from these rocks. Some granite masses contain disseminated columbite-tantalite, euxenite, or other niobium-tantalum-bearing minerals as primary rock constituents and in some places weathering and fluvial processes have concentrated these minerals into commercial deposits. Granite pegmatites are well known for their concentration of rare minerals, including minerals of niobium and tantalum, but the erratic distribution and small tonnage of these minerals in pegmatites commonly exclude pegmatites as a large source of supply. Even so, pegmatites are the principal source of the world’s tantalum.

Large low-grade deposits of niobium occur in alkaline rock complexes and related carbonatites in many parts of the world. Some multi-
millen-ton deposits are known in central Africa, southeastern Canada, Norway and Brazil, and at least five alkaline complexes with carbonates have been found in the United States. None has yet been discovered in Arizona.

Arizona Occurrences

Pegmatites have been the only commercial source of niobium-tantalum minerals in Arizona up to the present time. The most well-known niobium-tantalum-bearing pegmatites are in the White Picacho district in Mohave County, Arizona (Jahns, 1952) and in the Aquarius Cliff district of the Aquarius Range. These and other districts, mines, and prospects from which niobium-tantalum minerals have been reported are shown and listed in figure 36. The niobium-tantalum minerals have been recovered as byproducts or coproducts in mining beryl, feldspar, mica, and other pegmatite minerals in these areas and elsewhere (see "Beryllium," p. 102; "Feldspar," p. 342; "Lithium," p. 206; "Mica," p. 398; and "Rare earths and thorium," p. 245).

A typical pegmatite containing niobium-tantalum minerals is at the Rare Metals mine in the Aquarius Range. The deposit is one of a number of similar, subparallel pegmatites that cut the Precambrian granite of the area. The pegmatite is about 600 feet long and up to 40 feet wide and is well zoned with quartz, feldspar, and quartz-feldspar core zones and a distinct wall zone. Yttrium becomes a salient feature of the quartz core, and euxenite is found in the albite parts of the wall zone (Heinrich, 1960).

Outlook

The potential for large deposits of niobium or tantalum in Arizona is small. Although alkaline rock complexes and carbonates have not been found in Arizona, their occurrence in nearby states permits the possibility that they might yet be discovered in Arizona. If so, Arizona's potential for niobium would be enhanced. Meanwhile, small tonnages of niobium-tantalum minerals can be expected to be produced as byproducts of pegmatite mining, and where these minerals are recovered, they can add measurably to the value of the pegmatite ore.

Selected References


Figure 36.—Niobium and tantalum in Arizona.
PLATINUM-GROUP METALS

(By F. L. Stubbs, Arizona Bureau of Mines, Tucson, Ariz.)

INTRODUCTION

The platinum group of metals comprises platinum, palladium, rhodium, iridium, osmium, and ruthenium, of which platinum is the most important. Of these metals, osmium generally is alloyed with iridium and is referred to as osmiridium. The platinum-group metals occur chiefly as natural alloys of various proportions and to a lesser extent as sulfides and arsenides. All of these metals are rare, expensive, and possess individual properties that make them uniquely attractive for certain uses in highly developed technology and for use in jewelry and for decorative purposes.

Platinum and palladium are the most abundant and most widely used of the group; the other four metals are mainly used as alloy modifiers with platinum or palladium. High melting points, corrosion resistance, and catalytic properties of these metals have many industrial applications. In recent years the chemical, petroleum, and electrical industries accounted for about 80 percent of the platinum-group metals used in the United States (U.S. Bur. Mines, 1968, p. 112).

There has been minor production of the platinum-group metals from California and Alaska, but present domestic production, mostly from copper smelters, is insignificant when compared with domestic consumption. The platinum-group metals have important defense applications which has induced governmental restrictions on their use during wartime; platinum, palladium, and iridium are classified as strategic and are stockpiled (Ware, 1965, p. 717).

In 1966 the United States consumed 1,675,795 troy ounces and imported 1,435,017 troy ounces of platinum-group metals; the imports, valued at $85,410,000, were supplied by the U.S.S.R. (33 percent), United Kingdom (30 percent), Canada (11 percent), and other sources (26 percent) (U.S. Bur. Mines, 1967, p. 342–344).

Platinum-group metals are found mostly in geologic association with mafic and ultramafic rocks (peridotite, norite, dunite) or in placer deposits derived from primary sources. Important deposits of these metals are found in placers derived from ultramafic rocks in the U.S.S.R., in ultramafic igneous rocks of the Bushveld complex in the Union of South Africa, with nickel-copper ores of the Sudbury ultramafic complex in Canada, and in gold placers at Goodnews Bay, Alaska. Large deposits of these metals have never been found in the mafic and ultramafic complexes in the United States.

REPORTED OCCURRENCES AND OUTLOOK

Only a few occurrences of platinum-group metals have been reported in Arizona. These occurrences, however, are doubtful and the potential for finding platinum-group metals in Arizona is poor. Two small peridotite bodies occur in association with other lower Precambrian rocks in northeastern Maricopa County (Wilson and others, 1957), but no platinum-group metals have been found in them. About 1900, the discovery of large platinum deposits in the region of Cataract Canyon on the Colorado River was announced, but could not be verified (Blake, 1900). Several years later persistent reports of an occurrence near Indian Garden in the Grand Canyon led to several detailed examinations of the area by F. L. Ransome and H. G. Ferguson, and, though special care in sampling and assaying was used, no platinum was detected (Mining Sci. Press, 1919). Occurrences of platinum also have been reported in the San Domingo placers in Maricopa County, and near Prescott and near Columbia in Yavapai County (Galbraith and Brennan, 1959, p. 8). Columbia was a village on Humbug Creek west of the Tip Top mine and town (Granger, 1960, p. 329). However, no record of platinum production from these areas has been found, nor is there any record of platinum having been produced by buyers of gold from Arizona.

Erroneous reports of the presence of platinum-group metals often stem from the difficulties in detecting them. Assay for platinum and palladium, even for amounts that would constitute ore, is much more difficult than for gold. The other four metals in the group are even more difficult to determine. Even reliable and experienced assayers have been deceived into reporting nonexistent platinum. On the other hand, it is not likely to be missed if present and looked for. A new method for the determination of low concentrations of palladium, platinum, and rhodium (Haffty and Riley, 1968) may help alleviate this problem.

A number of metals and minerals have been metals are for platinum-group metals due to some of their properties. Among them are “chilled” birdshot (lead alloyed with arsenic), lead fragments from other sources, specular hematite in small flakes, and old amalgam. Any of these materials may be found in some panned concentrates, and if the sample has been roasted in the presence of carbon, metallic iron or other metals may have been formed. All of these materials may be surprisingly resistant to acid tests and even some gold-silver alloys are nearly insoluble in aqua regia.

Because of the difficulty in detecting the platinum-group metals and because of their probable scarcity in Arizona and elsewhere, caution is advised in accepting any unconfirmed reports of their presence.

SELECTED REFERENCES


RARE EARTHS AND THORIUM

(By J. W. Adams and M. H. Staatz, U.S. Geological Survey, Denver, Colo.)

INTRODUCTION

The rare-earth metals and thorium are hereby treated together as they are commonly associated in nature and are interrelated economically.

The rare-earth metals comprise the 15 elements having atomic numbers 57 to 71, including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). One of these elements, promethium, has been known only as an artificially produced isotope until its recently reported discovery in the rare earths recovered from apatite in Finland (U. S. Bur. Mines, 1965). Yttrium (Y), with atomic number 39, is also classified with the rare earths because of its chemical similarities and geochemical affinities.

The first seven elements listed above (La through Eu) are included in the cerium group of rare earths, so called because cerium is their most abundant member. The remaining eight elements (Gd through Lu), together with yttrium, are called the yttrium group. The two groups are also referred to, respectively, as the "light" and "heavy" rare earths.

The properties of the members of the two groups of rare earth elements are sufficiently distinct to cause one group to predominate over the other in most minerals, even though all or nearly all are ordinarily present.

OCCURRENCE AND USE

The rare earths are found in a large number of minerals, only a few of which have been found in sufficient concentration to be used as ores. One widely used source material is monazite, a rare-earth phosphate that is also an important ore of thorium. Another is bastnaesite, a rare-earth fluocarbonate, that has a slightly higher rare-earth content than monazite, but contains little or no thorium. Both monazite and bastnaesite contain predominantly cerium-group rare earths, but during the processing of these minerals, notably monazite, there is some recovery of yttrium-group elements. Minerals in which the yttrium-group elements predominate include xenotime, an yttrium phosphate, and a number of brown or black radioactive minerals, such as euxenite, samarskite, and fergusonite which are multiple oxides of yttrium, niobium (columbium), titanium, uranium, thorium, and other elements. Mina ble deposits of yttrium-rich minerals are uncommon, but xenotime has been obtained from a monazite placer at Aiken, S.C., and a multiple-oxide mineral, reportedly euxenite, has been recovered on a large scale, primarily for its niobium content, from placers at Bear Valley, Idaho. Yttrium is also recovered as a byproduct of uranium extraction plants treating ores from the Blind River-Elliot Lake deposits in Canada.

The rare-earth industry has developed largely around the cerium-group elements obtained from monazite and bastnasite, which are converted into a variety of products, including oxides and salts of the elements in varying degrees of purity, and misch metal which is a mixture of the rare earths in their metallic state.

For some industrial uses materials containing several of the rare earths as roughly separated fractions are satisfactory, others require products of high purity. The development of ion exchange and liquid-liquid solvent extraction techniques for the separation of rare-earth elements has made high purity metals and compounds available at greatly reduced cost. Within the past few years a good part of the industry has been devoted to supplying these purified materials primarily for use in electronic applications, notably as the red-producing phosphor used in color television tubes, and to a lesser extent in fluorescent lights. This phosphor, introduced in 1964, can be either europium-activated yttrium vanadate or europium-activated yttrium oxide (Chem. Eng. News, 1965). Adoption of the rare-earth phosphor has created an unprecedented demand for both yttrium and europium, domestic shipments of these in 1966 being about 125,000 pounds of yttrium oxide and 12,000 pounds of europium oxide (Chem. Eng. News, 1967).

Other important applications of the rare earths include the use of rare-earth oxides in glass polishing, rare-earth chlorides as catalysts in petroleum refining, oxides and fluorides in cores of carbon arc welding electrodes, and misch metal in sparking units and metallurgy. Minor amounts are used in ceramic glazes, in certain types of glass, and in synthetic garnets.

Rare earths produced in the United States are derived chiefly from bastnasite ore mined from a large carbonatite deposit at Mountain Pass in San Bernardino County, Calif. (Olson, and others, 1954; Evans, 1966). Additional amounts come from imported monazite and from stockpiled rare-earth-rich residues derived in the late 1950's from the processing of Idaho euxenite (f) for niobium.

Thorium is a heavy, soft, ductile, silver gray, radioactive metal. It is like uranium in that it is the parent of a series of radioactive decay products ending in the stable isotope of lead. Because of this characteristic, thorium is a potential source of atomic energy.

Thorium also has a number of minor industrial nonenergy uses, principally in thorium-magnesium alloys and gas mantles. Lesser quantities are used in refractories, chemicals, drugs, electrical, and electronic products. By 1965 two small prototype thorium reactors, one in Elk River, Minn., and the other in Peach Bottom, Pa., were producing electricity; other types were being developed (Baroeh, 1966, p. 918). Continued growth in the use of thorium in the electrical generating field appears promising. Rate of growth will depend on a considerable extent on the overall cost of generating electricity by thorium compounds versus that by uranium compounds.

Thorium produced in the United States in 1965 came from a beach sand placer in northern Florida containing monazite (Baroeh, 1966, p. 917). In 1965 the production of thorium throughout the world exceeded the amount consumed. Thorium was produced as a byproduct of uranium in the ores at Blind River, Canada, and as a
byproduct of rare earths in monazite. Until the use of thorium in generating plants develops, byproduct production will probably be able to furnish all the needs for this element.

**Arizona Occurrences**

Most of the thorium and rare-earth occurrences in Arizona are in pegmatites. These are commonly dike-like bodies that range from a few inches to thousands of feet in length. Most pegmatites are granitic in composition, having as their dominant minerals, quartz, feldspar, and mica, but are characterized by large but extremely variable grain size. Pegmatites are generally considered to represent the crystallization product of residual magmas and as such may contain concentrations of a number of elements whose properties inhibit their entry into the minerals of earlier formed rocks. The rare earths and thorium are among these elements and appear in pegmatites in a number of mineral species in which they are major constituents. Although these minerals may be valuable ore, their occurrence in pegmatites is generally too sparse to warrant their recovery. The occurrences of rare earths and thorium in Arizona are shown in fig. 37 and listed in table 20.

The most notable rare-earth-bearing pegmatite occurrence so far found in Arizona is that at the Rare Metals mine (Heinrich, 1960) in the Aquarius Cliffs area in Mohave County (fig. 37, locality No. 9) where several tons of yttrotantalite \((\text{Fe}, \text{Y}, \text{U})(\text{Nb}, \text{Ta})\text{O}_4\) were obtained during intermittent mining of the deposit. Other rare-earth and thorium minerals such as monazite, gadolinite, euxenite, allanite, and chevkinite have been found in pegmatites in the Aquarius Cliffs area (Kauffman and Jaffe, 1946; Galbraith and Brennan, 1959; and Heinrich, 1960).

A very large pegmatite mined for feldspar in the Cerbat Range about 5 miles north of Kingman (No. 6) contains allanite that is locally abundant in the footwall zone of the deposit. A partial analysis of this allanite showed that it contains 2.7 percent thorium (Heinrich, 1960, p. 10).

A pegmatite on the Mineral X claim (No. 7) near Kingman is noteworthy as being one of the few localities in the United States in which the rare yttrium silicate, thalcnite, has been found (Galbraith and Brennan, 1959, p. 99; Fabian and Woodhouse, 1964).

A black multiple oxide mineral, possibly euxenite, is found in small pegmatites in granite about 5 miles south of Buckeye in Maricopa County (No. 19). This mineral is found as minute crystals associated with smokey quartz, feldspar, biotite, magnetite, and sparse xenotime. Rare-earth-bearing pegmatites have also been found about 8 miles southwest of Buckeye.

Other pegmatites that reportedly contain rare-earth- or thorium-bearing minerals have been found in several localities in Arizona. These include the Cottonwood Creek area (No. 5), the Hillside and Quartz Mountain claims (No. 4), and the Signal district (No. 10) in Mohave County; the Peeples Valley mine (No. 14) in Yavapai County; the Ligurta district (No. 21) in Yuma County; Papago Wells (No. 23) in Pima County; and the Lucky Strike claim (No. 20) in Graham County.
Rare-earth minerals, most commonly monazite, may occur in concentrations in metamorphic rocks or in biotite-rich zones in igneous rocks. One such deposit has been found in the Virgin Mountains east of Mesquite, Nev. (No. 1) where a layer in Precambrian granite augen gneiss contains xenotime and monazite. A sample from this layer, which is 6 feet wide and has been traced along the outcrop for 100 feet, is reported by E. J. Young and P. K. Sims (1961, p. 274) to contain 5 percent xenotime and 2 percent monazite.

Vein deposits containing thorium and rare earths are known at eight localities. The largest of these is the Bechetti lease (No. 11) where a 3-foot-trending limonite-hematite quartz vein contains copper, rare-earth, and thorium minerals in this dike (Olson and Adams, 1962, p. 3). The vein is 25 feet wide and 1,000 feet long. Occurrences of rare earths and thorium are erratic but selected samples contained as much as 0.9 percent rare earths and 1.5 percent thorium. Four 8- to 9.5-foot chip samples contained between 0.02 and 0.43 percent thorium.

About 4 miles south of the Bechetti lease are the Farview claims (No. 12). Here a stockwork of mineralized fractures cuts green metavolcanics. This stockwork, which is 60 feet wide by at least 100 feet long, is filled with veinlets of quartz, limonite, hematite, siderite, dolomite, magnetite, and small amounts of thorite. Radioactivity of this stockwork is variable, but a 3-foot sample cut across the most radioactive part contained only 0.026 percent thorium. A second probable stockwork lies on the Valcarce claim (No. 17) near Cave Creek (Olson and Adams, 1962, p. 3). Here thorite was found in an altered area, 15 feet by 25 feet, in biotite granite.

Veins containing rare-earth and thorium minerals replace the country rock in two areas. One of these is in the Quijotia Mountains (No. 22), Pima County (Pabst and Thomassen, 1959; Williams, 1960) where quartz monzonite adjacent to mafic dikes has been changed to a rock made up mainly of albite with considerable epidote. The rare-earth- and thorium-bearing mineral, davudite, associated with sphene, calcite, chlorite, quartz, magnetite, fluorite, rutile, and anatase, is found locally in a zone 1 to 4 feet thick and about 100 feet long. The thorium content of the davudite is low, and a 4-foot long sample of the vein contained only 0.006 percent thorium. Allanite, a complex silicate containing rare earths, makes up 2 to 40 percent of another geologically similar deposit in the area. On the Uranium Basin claims (No. 8) in Mohave County, granite has been replaced in a 25-foot interval between a steeply dipping shear and a pegmatite. The thorium mineral, uranopherite, is found erratically scattered in this vein.

Small amounts of thorium and rare earths are found in three other areas. The Blendina claim (No. 3) has spotty radioactivity along the walls of a quartz vein cutting metamorphic rocks (Olson and Adams, 1963, p. 2). Radioactivity is due to monazite. The Willbanks prospect (No. 16), Yavapai County, is on a fine-grained mafic dike that cuts a fine-grained granite. Minor thorium is reported associated with limonite, hematite, and barite in this dike (Olson and Adams, 1962, p. 3). The Scott Lode (No. 18) in Yuma County near the town of Quartzsite is on a half-mile-long quartz vein cutting biotite schist. Radioactivity occurs in several small areas in the schist within 6 feet of the walls of the vein. Thorite was identified at one of these areas. The amount of thorium is small, however, as a 4-foot chip sample across the most radioactive area contained only 0.027 percent thorium.

Holocene and fossil placers are the principal source of rare-earth thorium minerals in many parts of the world. In Arizona, however, all known placers are small. Detrital monazite is found in crystals as much as 0.5 inch across in the Chehuenveis mining district (No. 13), Mohave County. It is sparsely scattered through stream gravels in an area of about 2 square miles (Overstreet, 1967, p. 115). A second placer of Holocene age is 11 miles southwest of the San Xavier Mission (No. 24) on the Cottonwood Ranch, Pima County. Here in an area at least several miles across, black sands in dry stream beds are slightly radioactive. The radioactivity is due to small amounts of allanite, which occurs principally with quartz, magnetite and lesser amounts of sphene, apatite, biotite, garnet, and zircon. In northeastern Arizona, in two placers 5 and 6 miles north of the Black Mountain Trading Post (No. 2) black sand laminae as much as 6 inches thick are exposed in sandstone of the Toerba Formation (Murphy, 1956, p. 5). These laminae are similar to the much larger titaniferous fossil placers occurring to the east, in western New Mexico, which also contain minor monazite.

One other occurrence of rare earths in sedimentary rocks has been reported (Gastil, 1954) near Diamond Butte in central Arizona (No. 16) where xenotime occurs in the outer part of ironstone concretions in the middle member of the Dripping Spring Quartzite.

**Outlook**

The general small size and low grade of the known thorium and rare-earth deposits in Arizona, together with much larger resources and higher-grade unworked deposits in other parts of the United States, suggest that little if any will be produced in the near future unless larger and higher-grade deposits are discovered.

Although not all rare-earth minerals contain sufficient thorium or uranium to be appreciably radioactive, radioactivity is still a most valuable guide to the discovery of rare-earth and thorium deposits. Deposits in layered metamorphic rocks, such as in the Virgin Mountains (No. 1), could be of economic interest if sufficiently rich and extensive, and they may be present but unrecognized in metamorphic
terrane elsewhere in the State. These deposits are best found and explored with the aid of radiation detecting equipment as they are apt to be otherwise indistinguishable from surrounding rocks.

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SILVER

(By Richard T. Moore and George H. Roseveare, Arizona Bureau of Mines, Tucson, Ariz.)

PROPERTIES, USE, AND MARKET CONDITIONS

Silver is a very ductile and malleable metal having a high specific gravity (10.5) and the capability of being polished to a high luster. Other physical properties of importance to industrial users include high electrical and thermal conductivity and the ability to alloy with other metals to form strong, high-temperature solders and brazing metals.

Silver has a long history of use and probably was one of the first metals worked by man—artifacts of silver have been found at archeological sites in Asia Minor dating from 3000 to 2500 B.C. (Ryan, 1965, p. 810). Because it is easily worked into attractive forms, one of the early uses for silver was in the fabrication of items of personal jewelry and objects of art, such as chalices and candelabra. This use persists to the present, and considerable quantities of silver are still used in silver plate, flatware, and jewelry.

Silver also has served as a base for monetary systems since early in its history. The Greeks used silver obtained from islands in the Aegean Sea for coinage in about 700 B.C., and the power and prestige of the city-state of Athens can in part be attributed to the wealth garnered from the silver mines of Laurium during the fifth century B.C. (Rickard, 1932, p. 554, 537). With the rise of the Roman Empire, that nation also established silver as a monetary base and it has been important ever since, both for coinage, and as a backing for paper currency. In 1934 the United States withdrew gold coinage from circulation and stopped its monetary use in domestic financial affairs. Silver was retained as the basis for its monetary system. As a part of this act, a guaranteed Treasury price for domestic mined silver also was established. As a result of this action and because the guaranteed price was higher than the world price, the Treasury became the major purchaser of domestic silver, and this situation prevailed until 1958. As a consequence, large stocks of silver in excess of monetary requirements were built up.

In addition to its use as a monetary metal, silver has many important industrial applications. In 1965, industrial consumption in the United States was 137 million ounces (U.S. Bur. Mines, 1967, p. 393). The use was distributed approximately as follows: 30 percent in the form of silver salts in the manufacture of photographic materials, 25 percent in the electronic and electrical industries, 12 percent in silver soldering and brazing alloys, 15 percent in the manufacture of such items as batteries, mirrors, missiles, and medical and dental supplies, and the remaining 18 percent in the arts for such things as jewelry and silverware (Eng. Mining Journ., 1966).

In the years following World War II, industrial consumption has steadily increased and the world price has increased apace. In 1958, when the world price reached the guaranteed Treasury price, the excess Treasury stocks were offered for sale, and by 1961 stocks in excess of monetary requirements had been exhausted and it was necessary to stop further sales. In the meantime, the consumption of silver in coins was also increasing, partly through the increased use of vending machines.

A comparison of production with monetary and industrial consumption of silver in the United States for the 1955-67 period (U.S. Bur. Mines, 1958-67, 1968) is shown in figure 38. Obviously, domestic production has not nearly kept pace with demand, and in recent years it has been necessary to import large quantities of silver. Important sources and percentage of imports during the 1963-66 period were Canada (33 percent), Peru (21 percent), Mexico (17 percent), Republic of South Africa (7 percent), and approximately 24 other countries (22 percent) (U.S. Bur. Mines, 1965; Ryan, 1965, p. 815). In 1965,
Congress, in an attempt to alleviate the critical silver shortage, passed legislation drastically reducing the silver content of our coins. The results of this action are clearly shown in figure 38. In spite of these efforts to relieve the silver shortage, however, U.S. consumption in 1867 was still more than six times as great as production.

Most domestic silver is produced as a byproduct of base-metal mining in the Western States and, consequently, the quantity produced is dependent upon base-metal requirements and is not particularly responsive to the demand for silver, as shown in figure 38.

**Production and History**

Arizona, with eight of the twenty-five leading silver producing mines in the Nation in 1960, has ranked second or third among the states in the production of silver since 1958, and the pattern of production in Arizona in recent years demonstrates the dependence of silver upon base-metal production. Since 1950, over 90 percent of the silver produced in the State has been as a byproduct of copper (80 percent), lead-zinc (10 percent), and complex copper-lead-zinc (4-5 percent) ores. In the past 20 years siliceous gold and silver ores probably have not accounted for more than 8 percent of the silver produced in Arizona in any single year.

Silver production in Arizona, however, has not always been dependent upon base-metal mining. “Bonanza” silver deposits had as much influence upon the early development of Arizona as did gold and, during the 1878-91 period, the value of silver produced exceeded that of gold by more than $28.9 million (Elsing and Heineman, 1936, p. 14). As early as 1850 Spanish explorers trekked northward from Mexico into what is now Arizona in search of silver and gold which were reported to occur in abundance in the Seven Cities of Cibola. According to most reports (e.g. Anderson and Creasey, 1958, p. 85), however, it was not until 1858 that Antonio de Espejo made the first discovery of silver ore in Arizona near the headwaters of the Verde River, probably at what was to be the future site of the United Verde base-metal mine. During the succeeding 125 years, Spanish expeditions intermittently penetrated into what is now Arizona but little is recorded concerning their mineral discoveries and only what can be considered legends have been passed down concerning these explorations.

According to an unpublished manuscript by J. B. Tenney, from which the following historical sketch largely has been abstracted, Padre Eusebio Francisco Kino, who for 30 years had been active in the development of the Papago Country, mentioned in his writings in 1705 the mining of rich silver ores, which were probably from deposits in the Santa Rita Mountains. With the exception, however, of the discovery of the famous Bolas de Plata silver deposit at Arizona in northern Sonora, in 1736, little mining activity occurred in the Arizona region and vicinity until 1825; the emphasis was on agricultural and religious development under the influence of the Spanish missionaries.

The year 1825 marked the entrance of the first American scouts into Arizona and the beginning of an era of intense prospecting for precious metals which lasted until the early 1890's. On the basis of reports that filtered out of the territory telling of the occurrence of rich mineral deposits, men such as the Pattee brothers and Paulene Weaver entered and prospected the northern part of the region, and in 1848 American troops under the command of Kearny were garrisoned in the southern part of the territory where many of the soldiers actively engaged in searching for precious metals. In 1854 Charles Poston began prospecting for gold and silver near Tubac and in 1856 the Santa Rita silver mine was opened in that area. As prospectors entered the region in ever increasing numbers, the tempo of exploration increased in the Santa Rita, Patagonia, and Cerro Colorado Mountains; the Mowry lead-silver mine in the Patagonia Mountains was discovered in 1858, and by 1859 the Heintzelman mine in the Cerro Colorado Mountains had been discovered and was yielding rich silver ore.

During the 1861-71 period, Federal troops were withdrawn because of the Civil War, and increased raiding by hostile Indians caused mining to almost cease. Typical of this period, the entire staff of the Santa Rita mine, with the sole exception of Raphael Pumpelly,
who narrowly escaped, was massacred. The raids continued until 1871, when Federal troops were again permanently stationed in the region and afforded the miners and settlers a measure of protection.

Between 1871 and 1878 many of Arizona's bonanza silver deposits were discovered. In 1874 Globe became an important silver camp, the Richmond Basin district north of Globe was opened, and the Mc Cracken silver mine in the Owens district, Mohave County, was discovered. The Silver King mine was located by Mason and Copeland in 1875 and in the same year the first claim was staked on the Magma vein, then known as the Silver Queen. In 1876 the United Verde ore body was discovered, or perhaps rediscovered, by M. A. Ruffner, and the rich lodes in the Wallapai district, Mohave County, which were first worked in 1864, were major silver producers. Also in 1876, Lieutenant Rucker and an army scout, William Dunn, of Fort Huachuca, made the first location in the Bisbee district on silver-rich iron cappings along the Dividend fault—although copper was known to be present in the district, it was of little interest at that time.

By 1879 silver was established as the major metal in Arizona. Tombstone, which had been discovered by Ed Schieffelin during the previous year, was a robust mining camp and for the next 12 years the bonanza silver deposits were the sites of booming mining communities. In 1882 over 5.8 million ounces of silver, more than that produced in any previous year, was mined (Elsing and Heineman, 1936, p. 15). According to J. B. Tenney (unpub. ms.) the Richmond Basin district produced over $3.5 million worth of silver between 1878 and 1893, and, in 1887 the Reymert mine, near Superior, produced 22,827 ounces of silver from 849 tons of ore (Blauvelt, 1889).

In 1893 silver was demonetized and prospectors turned their attention to gold. During the next few years the rich silver deposits played out, and after 1903 the bulk of Arizona's silver production came from base-metal ores, principally the large disseminated copper deposits. Siliceous gold-silver ore, and lead-zinc ore alternated in second place for a number of years, but the siliceous ores have not been important sources of silver since 1950.

In 1916 Arizona's silver production amounted to 7.2 million ounces and exceeded the previous record high, made in 1882, by 1.4 million ounces. Annual production since 1916 has ranged between 2.1 million and 9.4 million ounces (see fig. 39). Total production for the 1850-1967 period is estimated to be about 397 million ounces, valued at $324 million (Elsing and Heineman, 1936; U.S. Bur. Mines 1935-67; Larson and Henkes, 1968).

Types of Deposits

Silver has been produced in Arizona from deposits in 60 mining districts, or groups of districts, as shown in figure 40, and a brief geologic description of each is given in table 21. These deposits can be grouped geologically into three main classes: (1) siliceous vein deposits, with or without base-metal sulfides, (2) high-grade sulfide deposits, carrying principally either lead, zinc, or copper with silver as an accessory metal, and (3) low-grade disseminated copper deposits, in which silver occurs as a trace metal but from which it is economically recoverable, because of the large tonnages of ore treated.
Production in millions of troy ounces

1 Early production from oxidized zone of siliceous fissure veins in the Dividend fault zone. Veins contain silver chloride, native gold and silver, and some base-metal oxide minerals. More recent production from byproduct of massive copper sulfide replacement bodies localized along fault and fracture zone in Paleozoic limestone, and from the disseminated copper porphyry of the Sacramento and Lavender orebodies.

2 Argentiferous, lead-zinc and lead-copper sulfide replacement deposits in Paleozoic and Mesozoic limestone and large late-stage dikes. Anticlinal rolls in favorable host rocks acted as local traps for mineral-bearing solutions. Silver halide important in the oxidized, near-surface "bonanza" deposits.

3 Silver-copper sulfide replacement deposits along north-trending faults in Palaeozoic limestone and near east-west-trending fractures. Larger and better-grade deposits occur immediately above a diorite porphyry sill.

4 Irregularly shaped silver-lead replacement bodies in fissure veins and fractures and minor faults in Happy Limestone. High silver values restricted to oxidized zone, mostly in cerargyrite (silver chloride), possibly derived from oxidation of argentiiferous galena.

5 Silicous gold-silver-lead deposits in fissure veins and replacements, and lead-silver sulfide replacement deposit in Happy Limestone along north-trending faults, producing large and better-grade deposits occur immediately above a diorite porphyry sill.

6 Silver-silica replacement ore in fissure veins and replacement bodies in Tertiary andesite and rhyolite breccia.

7 Lead-silver and lead-copper-silver replacement deposit in irregular masses associated with monzonzitic to diorite dikes intrusive into Paleozoic limestone. Locally, pipes or chimneys of massive sulfides, 1 to 6 feet in diameter, follow fractures outward from the dikes in the limestone as much as 50 feet.
TABLE 21.—Silver Districts in Arizona—Continued

<table>
<thead>
<tr>
<th>Locality</th>
<th>County and district</th>
<th>Principal silver-producing mines, data of discovery(1), and years of principal production(2)</th>
<th>Mode of occurrence</th>
<th>References to mode of occurrence</th>
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<td>Cochise—Continued</td>
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<td>8</td>
<td>Don Cabres (Tevican)</td>
<td>Quarts veins containing small concentrations of gold and silver associated with base-metal sulfides, and contact metamorphic copper sulfide replacement bodies in Paleozoic limestone adjacent to diorite porphyry dikes which intrude the limestone along a zone of low-angle faulting.</td>
<td>Wilcox and others, 1930, 1950-55, p. 117-121; Atlas Bur. Mines file data.</td>
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<td>9</td>
<td>Cochise (Johnson)</td>
<td>Zinc-copper-silver and lead-silver minerals in both tabular and pipe-like replacement bodies. Deposits occur at intersection of easterly and northerly trending fractures with favorable shale and impure limestone beds of Paleozoic age. The majority of the ore bodies are parallel to the bedding; a few are sub-parallel to the intersecting fractures.</td>
<td>Cooper, 1950.</td>
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<tbody>
<tr>
<td>22</td>
<td>San Francisco (Yuma)</td>
<td>United Eastern, Tom Reed, Gold Reef (ca 1860), 1903-4</td>
<td>Silica-cemented gold-flourite veins carry low silver values. Veins strike north-northeast and have vertical dip.</td>
<td>Ranome, 1923; Wilson and others, 1934, p. 80-100.</td>
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<tr>
<td>24</td>
<td>Wallapal (Chiricahua, Cerrillos, Mineral Park, and Stockton)</td>
<td>Numerous mines (ca 1860), 1864-1917, 1925-40, Ithaca Peak, 1944-6</td>
<td>Early production from near-surface bonanza silver-chloride deposits in locally dipping silica-cemented veins that trend either northerly or N. 60° W., and cut Precambrian igneous and crystalline metamorphic rocks. Later production from lead-silver-sulfide deposits in the deeper parts of the veins. Recent production is byproduct from disseminated copper porphyry in Ithaca Peak Granite.</td>
<td>Schrader, 1909, p. 49-108; Seng, 1950; 1951.</td>
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<td>25</td>
<td>White Hills</td>
<td>Numerous mines (1892), 1892-1906</td>
<td>Quartz veins contain silver chloride and, locally, much manganite and iron oxide. The veins, which average about 3 feet in width, are in Precambrian granite gneiss, strike west-northwesterly, and dip 20°-40° MS. Higher silver values apparently were restricted to altered parts of veins.</td>
<td>Schrader, 1909, p. 127-135.</td>
</tr>
<tr>
<td>28</td>
<td>Cobre</td>
<td>Several small producers (ca 1850), intermittently.</td>
<td>Silver-lead-gold minerals in fissure veins in granite and andesite flows.</td>
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<td>31</td>
<td>Baheswari</td>
<td>Allarne, Iowan, Gold King (ca 1890), 1895-98, intermittent since 1928.</td>
<td>Silica-cemented gold-silver fissure veins in unmetamorphosed to slightly metamorphosed Cretaceous (?) shale, conglomerate, and quartzite. Veins intruded by dikes of granite and diorite porphyry. Veins dip from 15 to 90 degrees, High-grade silver occurs in areas containing abundant manganite and iron oxide.</td>
<td>Wilcox and others, 1934, p. 100.</td>
</tr>
<tr>
<td>34</td>
<td>Empire</td>
<td>Total Wreck (1879), 1880-86, 1907-10, 1913-25.</td>
<td>Lead-silver-copper minerals in replacement deposits in brecciated Paleozoic limestone adjacent to faults and fractures that trend east and N. 30° E. Silver values decreased rapidly with depth.</td>
<td>Wilson, 1951b.</td>
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**TABLE 21.—Silver Districts in Arizona—Continued**

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**References**

Silver has been produced from siliceous vein deposits at several localities in Arizona, and these veins fall into two principal categories: (1) epithermal gold-silver-quartz veins, and (2) mesothermal gold-silver-quartz veins.

Representative of the epithermal veins are the deposits in the Oatman and Katherine districts, Mohave County (fig. 49, Nos. 22 and 23). The metallic ore minerals consist of free gold, alloyed with some silver, and minor amounts of pyrite and occasional blebs of chalcopyrite. Gangue minerals are mainly quartz and calcite with lesser amounts of adularia. Fluorite occurs sparingly in some of the deposits. The vein material occurs in some places as the filling in simple fissures from a few inches to a few feet wide, and in other places as stringers and discontinuous veinlets in zones a few feet to 60 or 70 feet wide. Higher gold and silver values are frequently found associated with iron- and manganese-stained quartz, and in vugs, pockets, and breccia zones containing iron and manganese oxides. Tertiary volcanic flows are the host rocks for the veins.

Mesothermal veins were important sources of silver in several districts in the Bradshaw Mountains (No. 47) in south-central Yavapai County, in the White Hills district (No. 25), Mohave County, and the Dos Cabezas (No. 8), Cochise County, and Fortuna (No. 60), Yuma County. The mineralogy of these deposits generally is simple. The metallic minerals include free gold and silver and small amounts of argentiferous galena, sphalerite, chalcopyrite, and pyrite; quartz is the most important and generally is the only gangue mineral. In general, these veins are simple fissure fillings with smooth walls and regul-
lar tabular shapes. Host rocks are predominantly Precambrian granite, gneiss, and schist, although Paleozoic sedimentary rocks and Mesozoic intrusive rocks contain some vein deposits thought to be of this category.

**BASE-METAL SULFIDE DEPOSITS**

Notable quantities of silver have been produced from deposits which are primarily important as either lead, lead-zinc, or zinc-copper deposits. These occur as fissure veins, replacement bodies of massive sulfide minerals, and tectite replacements.

Argentiferous base-metal fissure veins are prevalent in Yuma County in the Castle Dome (No. 58) and Silver (No. 59) districts. Metallic minerals include argentiferous galena, sphalerite, chalcopyrite, and pyrite. Gangue minerals consist of various combinations of calcite,ankerite, siderite, barite, fluorite, and quartz. The vein material fills fissures in faults and breccia zones, and may be continuous along strike for several thousand feet or may occur as discontinuous lenses and shoots. Generally the host rock is igneous or metamorphic. Where base-metal fissure veins cut sedimentary rocks, such as the deposits in the Tyndall (No. 41), Harshaw (No. 42), and Patagonia (No. 43) districts, in Santa Cruz County, they commonly grade into veins containing mainly sulfide minerals and massive sulfide replacement deposits consisting mainly of galena, and sphalerite, or sphalerite and chalcopyrite.

Silver also is associated with lead, zinc, and copper in tectite replacement bodies. These contact metamorphic deposits generally are found in Arizona as replacements in Paleozoic limestones close to granitic intrusive masses and consist of metallic sulfides, such as galena, sphalerite, and chalcopyrite, disseminated in a silicate mixture composed of garnet, diopside, epidote, and various amphibole and pyroxene minerals. Some of the deposits in the Cochise (No. 9), Silver Bell (No. 29), and Pima (No. 33) districts are representative of this type.

The high-grade or "bonanza" silver deposits, which were so productive during the 1871-87 period, resulted from the oxidation and supergene enrichment of silver-rich base-metal deposits of the fissure vein and replacement types. As a rule, the high silver values were restricted to the upper parts of the deposits, including the oxidation zone (extending from the water table to the surface), and the enrichment zone (at and just below the water table). The Tombstone (No. 3) and Wallapai (No. 21) districts are representative of the "bonanza" deposits.

**DISSEMINATED COPPER DEPOSITS**

Since about 1916, the major production of silver in Arizona has come from the large copper- porphyry deposits such as Morenci (No. 17) and San Manuel (No. 56) (see Copper, page 139). The average silver content of the disseminated copper ores in 1965 was only slightly more than 0.05 ounce per ton of ore, or 0.2 ounce per ton of copper produced. However, the total silver produced from these ores in 1965 amounted to over 5.3 million ounces (Larson and Henkes, 1967, p. 96).

**SUMMARY AND CONCLUSIONS**

As indicated above, silver production in Arizona during the last few decades has been directly related to base-metal mining, particularly copper, and there is every indication that silver produced as a byproduct of copper mining will continue to account for a large part of the State's output. However, the demand for silver is steadily increasing and extensive exploration programs have been undertaken within recent years. Although no significant new deposits of silver have yet been found in Arizona, a good potential for new discoveries does exist, and a possible key to their discovery may be found in a comparison of the distribution of deposits of silver with those of lead.

Similar to the distribution of lead deposits in Arizona (fig. 27), silver deposits occur in a broad belt extending northwesterly from Cochise and Santa Cruz Counties to Lake Mead on the northwest border of Mohave County (fig. 40). Also, a similarity in the clustering of the deposits is apparent within the belt. A large concentration of deposits occurs in central Yavapai County, where numerous fissure veins containing lead-silver deposits intersect Precambrian igneous and metamorphic rock (see "Geologic map," fig. 3), and a second concentration of deposits is centered in Santa Cruz, western Cochise, and southeastern Pima Counties where the more important deposits consist of massive lead sulfide replacements in Paleozoic and Mesozoic sedimentary rocks and from which silver was produced either as a cop product or an important byproduct. This latter area is considered to be particularly favorable for further prospecting because of its potential for containing significant concealed deposits, either beneath the alluvium flanking the mountain masses, or beneath postmineral volcanic rocks which cover extensive areas in parts of the region.

**SELECTED REFERENCES**


INTRODUCTION

Cassiterite (SnO₂), a heavy dark-brown to black tin oxide, is the only tin-bearing mineral of commercial importance. The United States is the world’s largest user of tin and is totally dependent upon foreign sources of supply; thus, tin is designated a strategic material, and stockpiled. Principal uses are in tinplate, soft solders, bronze and brass, babbitt, and type metal. About 62 percent of the known world tin reserves are in Southeast Asia (U.S. Bur. Mines, 1968, p. 152) and in 1967 imports into the United States came principally from Malaysia and Thailand.

The major commercial tin deposits of the world occur in placers derived from weathering and erosion of cassiterite-bearing, felsic, phaneritic igneous rocks such as granite and quartz monzonite. Although Arizona has abundant occurrences of similar plutonic igneous rocks, only two occurrences of cassiterite have been reported.

ARIZONA OCCURRENCES

Jahn (1952, p. 49) reported rare cassiterite crystals in some of the pegmatite bodies in the White Picacho district of Maricopa County where it occurs in fractured and brecciated quartz, especially in the


--- 1951, Geology (Mount Dana mine), in Arizona zinc and lead deposits, Mining World, v. 16, chap. 158, p. 43-49.


--- 1959, Mining World, v. 21, no. 1, p. 32-35.


--- 1954, Structure and mineralization at Superior, Arizona: Mining Eng., v. 6, no. 11, p. 1015-1019.


Outpost pegmatite in NE 1/4 sec. 3, T. 7 N., R. 3 W. This tin occurrence is more of a mineralogical curiosity than a deposit with commercial possibilities.

Galbraith and Brennan (1959, p. 32) reported the occurrence of cassiterite about 25 miles east of Safford, Graham County, approximately in the SW 1/4 of sec. 31, T. 7 S., R. 30 E., and in the W 1/4 sec. 6, T. 8 S., R. 30 E. Some of the occurrence is exposed in road cuts of U.S. Highway 70 which cuts diagonally through the area. Cassiterite occurs with hematite as low-grade disseminations and as narrow veins in fractures in rhyolitic volcanic rocks. Scattered nodules of cassiterite have been found on hilltops and in washes. Prospecting has been limited to the examination and sampling of road cuts and trenches. Although the occurrence is interesting, studies have not encouraged more extensive exploration efforts.

OUTLOOK

The possibility of discovering commercial tin deposits in Arizona is remote, but possible. Exploration efforts generally have been directed toward finding metals of more common occurrence and have not specialized on the search for tin. The U.S. Geological Survey has initiated a study of domestic resources of certain heavy metals, including tin, and additional information on the occurrence and distribution of tin in Arizona may result from this program.

SELECTED REFERENCES


TITANIUM


INTRODUCTION

Titanium is the ninth most abundant element in the earth's continental crust, constituting about 0.6 percent. Its greatest use has been as titanium dioxide in pigments, but in recent years titanium metal has been utilized at an increasingly greater rate than pigments. Its use as a structural metal was only made possible by advances in metallurgy which followed World War II. The United States consumed about 1.1 million short tons of TiO₂ concentrates in 1962 and 1963, divided (in 1963) as follows: 96.8 percent in pigments, 1.5 percent welding rod coatings, 1.4 percent as metal, and 0.3 percent for other purposes including use as a ferroalloy and carbide and use in plastics and ceramics (Peterson, 1966).

An increased consumption of about 5 percent a year should continue through 1980 for TiO₂ pigment and 10-15 percent a year through 1970 for titanium metal (Stamper, 1965, p. 988). By the end of 1980, the domestic consumption of TiO₂ pigment is expected to be 1.2 million short tons and titanium metal 70,000 short tons (Stamper, 1965, p. 988).

Titanium dioxide was developed as a pigment for paints because of its high opacity, its chemical and physical stability, and its low specific gravity. By 1963, in the United States, titanium dioxide base pigment far exceeded the production of all other white pigments combined (Stamper, 1965, p. 972).

Titanium is the fourth most abundant structural metal, has the highest strength to weight ratio of any of them, shows little change in physical properties from minus 300° F. to 1,000° F., and has the greatest resistance to corrosion of any common metal or alloy (Schlairn, 1964). These properties explain its increasing use in supersonic jet aircraft, rockets, submarines, desalination plants, and elsewhere in industry where extreme temperatures or corrosion are major problems.

The principal economic minerals of titanium are rutile (TiO₂) and ilmenite (FeTiO₃). United States production of these minerals in 1963 was 890,000 short tons of ilmenite and 11,900 short tons of rutile (Stamper, 1965). Both rutile and ilmenite are found in primary or lode deposits in igneous or metamorphic rocks and in alluvial or eluvial deposits, including placers, beach sands, saprolite, and bauxite. The principal ilmenite deposits, however, are primary, and are associated with anorthosite-gabbro complexes, whereas most of the world's rutile is obtained from beach sands. United States ilmenite production is from anorthosite deposits in New York, saprolite in Virginia, and beach sands in Florida and New Jersey. Rutile is produced from saprolite in Virginia and beach sands in Florida. Anatase (TiO₂) and other alteration products of ilmenite are also recovered from some placer deposits.

ARIZONA TITANIUM RESOURCES

Arizona has no known economic deposits of titanium. There are occurrences of low-grade rutile, ilmenite, titaniferous magnetite, and titaniferous hematite that do not appear to be economic under present-day market conditions. Only two notable concentrations of rutile are known, one in Santa Cruz County and the other in Yavapai. In Santa Cruz, 3 miles southwest of Duquesne, rutile has been found as a late hydrothermal mineral in a pegmatite dike cutting altered diorite (Moore, 1953, p. 13). The rutile is associated with pyrite and molybdenite. The tenor of rutile in copper ore from Bagdad, Yavapai County, has been calculated at about 6 pounds per ton (Anderson and others, 1955, p. 97). Because of the large amount of material handled in the copper operation, this occurrence has been mentioned as a possible source of rutile, but because of the small size, the rutile crystals are not economically recoverable.

Ilmenite is of far greater importance than rutile as a titanium resource in Arizona. In a recent survey of titanium resources of the United States, Peterson (1966, p. 11-12) lists two Arizona ilmenite deposits but notes that the fine-grained nature of the ilmenite, as well as its intimate association with magnetite and hematite, made it impractical to beneficiate. These occurrences are shown in figure 41 and table 22. With large, relatively high-grade ilmenite deposits as yet undeveloped in California, Wyoming, and elsewhere in the United
TABLE 22.—Titanium occurrences in Arizona

<table>
<thead>
<tr>
<th>Locality</th>
<th>County and</th>
<th>Titanium minerals</th>
<th>Geology of occurrence</th>
<th>Percent content</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cochise</td>
<td></td>
<td>Ilmenite</td>
<td>With magnetite and specular to earthy hematite in copper ore; contact metamorphic replacements of Paleozoic limonite near granitic intrusives.</td>
<td>44.6</td>
<td>Harrer, 1964, p. 22-24.</td>
</tr>
<tr>
<td>Gila</td>
<td></td>
<td>Ilmenite</td>
<td>With hematite and iron ore in Upper Cretaceous formation (Permian). 1,000 feet thick and over 2.5 miles long, as a sheet-quartz-iron sandstone member.</td>
<td>39.0</td>
<td>Harrer, 1964, p. 52-54.</td>
</tr>
<tr>
<td>Iron King group</td>
<td></td>
<td>Ilmenite</td>
<td>Place deposits ranging from a few feet to more than 100 feet thick, covering 6,000 acres; magnetite and ilmenite constitute 3-7 percent of alluvium.</td>
<td>20.8</td>
<td>Harrer, 1964, p. 71-72.</td>
</tr>
<tr>
<td>Marnita</td>
<td></td>
<td>Ilmenite</td>
<td>Occurs in Precambrian quartz-silt schist and pegmatite as intergrowths up to 1/2 inch in diameter and segregation up to several inches in diameter.</td>
<td>5.6</td>
<td>Harrer, 1964, p. 71-72.</td>
</tr>
<tr>
<td>Maricopa</td>
<td></td>
<td>Ilmenite</td>
<td>Alluvial deposits with disseminated and stratified magnetite deposits, occur in about 600-mile-square area.</td>
<td>20.8</td>
<td>Harrer, 1964, p. 71-72.</td>
</tr>
</tbody>
</table>

EXPLANATION

Titanium occurrence

(Number refers to locality listed in table 22)

FIGURE 41.—Titanium in Arizona.
States, there appears little likelihood that any of the Arizona occurrences will be exploited within the next two decades, except in the event of a national emergency. However, since placers with iron and titanium minerals have been found in many places, it is possible that economic ilmenite placer deposits also exist. On the other hand, with no known anorthosite bodies in the State, the chances of a large titanium lode deposit being found are slight.

Selected References


Tungsten

(Ty S. W. Hobbs, U.S. Geological Survey, Denver, Colo.)

Properties, Use, and Market Conditions

Tungsten is a metal whose strategic value depends mainly on the unusual physical and mechanical properties of the element, its alloys, and certain special compounds. In pure form, tungsten is light gray, very heavy, and has the highest melting point of the metals, about 3,410°C (6,170°F). Tungsten alloys and carbides are notable for their extreme hardness and wear resistance, and particularly for retaining hardness at elevated temperatures.

Pure or nearly pure tungsten metal is important in electric lighting, electronics, and electrical contact applications. However, over 70 percent of domestic consumption is in alloy tool steel and tungsten carbide used for cutting edges, dies, drill bits, wear-resistant machine parts, tire studs and other applications where extreme hardness is desirable. Some is also used for high temperature applications in various aspects of space technology.

U.S. consumption in 1960 was 13,868,000 pounds of contained tungsten. Domestic mine shipments totaled 7,566,000 pounds, and imports for consumption 3,918,000 pounds (U.S. Bur. Mines, 1965). Although the U.S. tungsten mining industry has operated continuously (except for 1921 and 1922) for over 60 years, the rate of production has ranged widely as a result of price fluctuations. Quotations for domestic tungsten in 1904 were $16 to $19 per short ton unit of WO3, in contrast to a Government stockpile price of $63 in 1951-52 and a war-induced price of $35 in 1916. The price throughout 1967 was $43 per unit. Output is quite sensitive to price, and at the lower rates prevailing since 1956, few tungsten mines in the United States have been able to compete consistently on the open market with foreign producers (Stevens, 1965, p. 1001). However, a large domestic productive capacity was demonstrated twice in the last 25 years under conditions of special need or incentive: in 1943-45, to fill heavy demand of the war effort; and between 1950 and 1956 under the influence of the price incentive of the Government stockpiling program during the Korean crisis. In 1955, production reached an all-time high that was nearly four times the average annual production of the immediate postwar period, 1946-50. In 1956, nearly 600 producers reported some production; in 1958, after the removal of Government price support, only two producers were active (U.S. Bur. Mines, 1956, p. 1227, and 1959, p. 1081). These data illustrate dramatically the fact that the United States has a substantial supply of tungsten available if the need warrants the price that is necessary to extract it.

Manner of Occurrence

Tungsten minerals are widely distributed in various rock types of the earth’s crust, but for the most part are genetically associated with igneous rocks of granitic composition. About 14 minerals contain tungsten as an essential component, but of these the only commercially important ones are those of the wolframite group, ferberite, FeWO3,
wolframite, (Fe, Mn)WO₄, and huebnerite, MnWO₄, and scheelite, CaWO₄. Although the wolframite group is economically most important in the world as a whole, scheelite has accounted for nearly three-fourths of the U.S. output.

U.S. deposits include: quartz veins that contain minerals of the wolframite group, scheelite, or both; contact-metamorphic deposits containing scheelite in association with garnet and other silicates formed at places along contacts of granitic intrusive rocks with invaded limestone; and disseminated hydrothermal deposits of scheelite and wolframite associated with other economic minerals in igneous, sedimentary, and metamorphic rocks. Some tungsten-bearing minerals have also been found in pegmatites and as concentrations in placer deposits. In a few places, tungsten-bearing iron and manganese oxides have been worked, as at Golconda, Nev.

Most tungsten ores contain only small amounts of the common tungsten minerals. The content of WO₃ in ores mined for the metal has ranged from 0.25 percent to more than 10 percent, but the average is probably between 0.5 and 1.0 percent. At the Climax molybdenum mine in Colorado, huebnerite, which is present in parts of the great molybdenum ore body in amounts far below the grade that could be mined for tungsten alone, is produced as a byproduct. Because of the very large tonnage of ore processed, the Climax mine is one of the leading producers of tungsten concentrates in the country.

To meet requirements for sale and utilization, most tungsten ores must be concentrated to 60 to 70 percent of WO₃ before utilization. The concentrate also must meet low tolerances of such impurities as tin, copper, arsenic, antimony, bismuth, molybdenum, phosphorus, sulfur, lead, and zinc, each of which may be injurious for particular uses. Scheelite (calcium tungstate) forms a gradational series with powellite (calcium molybdate) and may contain varying proportions of molybdenum and tungsten. Some scheelite concentrates, especially from contact-metamorphic ore bodies, contain as much as 5 percent of molybdenum chemically combined in the scheelite. The molybdenum must be removed by chemical digestion if a molybdenum-free product is required.

**HISTORY AND PRODUCTION**

The first report on tungsten in Arizona was made in 1896 by W. P. Blake, Territorial Geologist. Huebnerite was identified from veins of Bluebird Hill in the Little Dragoon Mountains in 1898, and the first production of tungsten ore in Arizona was apparently from this district in 1900. The discovery of most of the more important deposits followed soon thereafter; the Las Guijas district in 1899, Boriana and Campo Bonito districts sometime before 1908, and the Huachuca Mountain area in 1916. Nearly 200 small mines, prospects, and mineral occurrences have been found in Arizona since the early discoveries all of which are in the southwestern half of the State. The high plateaus of northeastern Arizona are notably devoid of tungsten minerals.

The total production of tungsten from Arizona from 1900 to 1965 is estimated at about 280,000 short ton units WO₃ (a short ton unit is equal to 1 percent per ton or 20 pounds). The State ranks sixth in the country in total production for the period 1900 to 1957 (Holliday, 1960), and contributed during this time 2.27 percent of the national output. The Boriana, Campo Bonito, Little Dragoon Mountains, Las Guijas, and Huachuca districts have contributed the great bulk of this production; of this production, the Boriana mine has yielded more than the combined output of the rest of the State.

**ARIZONA DEPOSITS**

Tungsten minerals in Arizona have been found in a variety of modes of occurrence, but all of the production to date has come from quartz veins and irregular replacements in metamorphic and plutonic rocks and in small amounts from placer deposits in the Little Dragoon and Camp Wood districts. Small amounts of scheelite have been reported in talcite at Johnson (Hess and Larsen, 1922) and at other places in the State, but none has been mined. Tungsten has also been detected in small amounts in manganese minerals that form small veins in granite, conglomerate, and Tertiary volcanic rocks (Hewett and Fleischer, 1960).

The location of most of the tungsten districts, mines and prospects from which some production has been reported are shown in figure 42, and of these the 15 more important ones are listed and identified by map number. More than 80 other occurrences are shown but not identified. Much of the information on the location, production, and geologic relations of tungsten deposits in Arizona has been taken from the excellent bulletin by Wilson (1941), from the Mineral Resource Map on tungsten in the United States by Lemmon and Tweto (1962), and from the detailed compilations of information on tungsten occurrences in Arizona by Dale (1959, 1961), and by Dale, Stewart, and McKinney (1960).

Most of the deposits, including several of the more productive ones, occur in igneous and metamorphic rocks of Precambrian age. A few are localized along faults between the Precambrian complex and Paleozoic rocks or in the Paleozoic rocks, whereas a few others are in intrusive bodies related to the Laramide orogeny. The tungsten in manganese minerals is in veins some of which are known to cut Tertiary sediments and lavas. Although a definite age of mineralization has not been established for most of the tungsten deposits in Arizona, and the geologic relations permit a wide range of time from Pre cambrian to Tertiary, most of the deposits are considered to be related to igneous rocks that were intruded during the Laramide orogeny. At the Boriana mine in Mohave County (No. 1, fig. 42), both wolframite and scheelite occur in narrow quartz veins that follow the foliation of an elongate roof pendant of phyllite in granite. These veins, by far the most productive to date in Arizona, have been described in detail by Wilson (1941) and Hobbs (1944). Most of the production came during the period between 1915 and 1943 and totaled about 139,000 units WO₃. From 1951 through 1956 about 10,000 additional units were produced, some from the mining of pillars and extraction of old stope fill, but most from the reworking of about 135,000 tons of dump material (Dale, 1961). Most of the accessible ore has apparently been mined and the extremely unstable character of the phyllite country rock together with the flooding of the lower mine levels has led to the collapse of most of the extensive workings in recent years.
Additional tungsten production from the Boriana mine is unlikely although other small mines and prospects in the district may continue to yield small amounts.

In the Campo Bonito district in Pinal County (No. 4, fig. 42) scheelite occurs in faults and shear zones closely related to the Mogul fault and subsidiary structures that separate Precambrian granite on the north from upper Precambrian and Paleozoic sedimentary rocks on the south. The highest concentrations of the ore are localized in fractures and breccia zones that intersect limestones or impure carbonate-bearing layers in the sedimentary sequence (Wilson, 1941). Three mines, the Bonito (Maudina), Pure Gold and Morning Star have produced most of the ore from the district which totals nearly 25,000 units of WO₃.

The Las Guijas district in Pima County (No. 7) includes a series of tungsten-bearing quartz veins that cut granite within an area about 3 miles long and half a mile wide. These veins contain local concentrations of huebnerite, pyrite, chalcopyrite, sphalerite, and galena, and occasionally a little scheelite. The veins range in thickness from a few inches to 20 feet, and pinch and swell along the strike and dip. In places they occupy the same fractures with lamprophyre dikes. The huebnerite ore shoots are irregular and apparently shallow, and are separated by long stretches of barren veins. The more important mines include the General Electric group of veins, Pauli vein, Zappia group, and a few others. Total production has been in excess of 20,000 units.

Veins similar to these in the Las Guijas district constitute two parallel vein zones in the Little Dragoon Mountains in Cochise County (No. 5). These zones, each from 150 to 1,000 feet wide, are composed of a number of narrow veins containing sporadic tabular crystals or blocky masses of huebnerite that range from a fraction of an inch to several inches in diameter. The huebnerite ore occurs in small shoots of irregular shape, size, and distribution. Most shoots measure only a few feet horizontally and vertically. No vein has been explored to vertical depths of more than 150 feet, probably because the surface workings were not profitable enough to encourage deeper exploration. An estimated 25,000 units have been produced from this area. About half of this production came from surface placer deposits northeast of Bluebird Hill. The erratic distribution and generally small size of the ore shoots in the widely scattered veins of this district, will probably always restrict production to small intermittent operations.

About 12,000 units of WO₃ have been produced since 1916 in the Huachuca Mountains, Cochise County—almost all from the Tungsten Reef mine (No. 6). Scheelite ore containing from 0.9 to 1.0 percent WO₃ is found in irregular shoots within a quartz vein that follows bedding in the Abrigo Limestone. Quartz outside of the ore shoots is barren except for local traces of scheelite. Small concentrations of scheelite have been found in many other quartz veins in the Huachuca Mountains and some have been productive.

**Outlook**

Tungsten minerals, in most occurrences, are characteristically erratic and spotty in distribution, and the controls that localize the ore shoots are obscure and poorly understood. This generally is as true of the few
large continuous ore shoots (as at the Boriana mine) as it is of the more usual small shoot, pocket, or mineral grain. The erratic pattern of ore distribution seems to be more pronounced in quartz veins and the related shear zone replacements and deposits in silicified breccias than in the contact metamorphic type of deposit. Because of this characteristic, the future of the predominantly quartz vein tungsten province of Arizona is difficult to evaluate. At times of favorable prices, the known pockets of ore are usually mined out, and the vague guides to new discoveries together with the high cost of development have discouraged exploration for new ones. As a consequence, a valid measure of ore reserves is nearly impossible—even for districts with a significant and long history of production. However, the potential for future production is probably greater in such well known districts than among the multitude of small mines and prospects that dot the State. Arizona has made significant contributions to the National production of tungsten in the past. The depletion or near depletion of several of the major producers, however, has reduced the potential for future significant production. The great host of small mines and prospects can be counted on for small intermittent output at times of great demand, but a revival of a steady tungsten mining industry must depend on new discoveries of major size. Predictions for such discoveries are hazardous at best for most mineral commodities, but especially so for one with such erratic behavior as tungsten. Deliberate exploration for new sources would probably be best advised in areas of known concentrations in the search for extensions of well-known veins, and on new structures that bear similarities to known productive ones nearby. The success of the byproduct recovery of very low-grade huebnerite at Climax, Colo., points up the need for an awareness of possible similar occurrences in any large-scale mining operation being operated primarily for some other commodity.

SELECTED REFERENCES


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URANIUM

(By A. P. Butler, Jr., and V. P. Byers, U.S. Geological Survey, Denver, Colo.)

INTRODUCTION

Uranium is a metallic element of growing importance as a source of atomic energy. The natural element is a mixture of three isotopes, U234, U235, and U238 which make up 90.28, 0.71, and 0.005 percent, respectively, of the mixture. The nucleus of the isotope U235 (fissions) splits readily, and the U238 isotope is converted by neutron capture to an isotope of plutonium, Pu239, which is also fissionable. The fissioning of these isotopes yields a very large amount of energy per unit weight. This energy can be released explosively, which makes uranium very significant for military uses and potentially significant for fracturing a large volume of rock or it can be released slowly so that uranium is of rapidly growing importance as a source of sustained power. From 1949, when a self-sustaining nuclear reaction was first demonstrated, until about 1965, uranium was used or stockpiled to meet military requirements. Recently, however, it is in increasing demand as a fuel for generating electricity. More than half the large electric generating plants ordered in 1966 will use nuclear power and uranium fuel. A small amount of uranium is used in ceramic, chemical, and electrical industries.

Uranium is widely distributed in the United States in rocks of many types and ages, but the principal deposits are in continental sedimentary rocks. Most are in sandstone but some are in conglomerate, limestone, and coal or carbonaceous rocks. A few important mines are in marine black shale, and some marine phosphate rock and some marine phosphate rock contain very large quantities of uranium dispersed as a very small fractional constituent of the rock. Summary descriptions of different occurrences are given by Page, Stocking, and Smith (1956), Butler, Finch, and Twenhoefel (1962), Vine (1962), Walker and Osterwald (1963), and Finch (1967).

HISTORY AND PRODUCTION

For about 25 years the United States has been the principal user of uranium. From 1949 through 1966, 301,060 tons of U3O8 have been acquired, of which 154,460 tons came from domestic ore and the rest from foreign areas, mainly Canada and Africa. Arizona's contribution up to the end of 1966 was 9,291,000 tons of ore containing 8,400 tons of U3O8 and the State ranks fifth among the States in total ore production, the value of which is estimated to be about $74.4 million. The value of the contained U3O8 in mill concentrates is about $141.6 million but as only one uranium recovery mill has operated in Arizona, much of the ore mined in the State was shipped to mills in Utah, Colorado, and New Mexico for treatment. In terms of value realized in the State, uranium ranks in sixth place among the metals recovered during the period 1948 through 1966.

1 Data furnished by the Ore Reserves Branch, U.S. Atomic Energy Commission, Grand Junction, Colo.
Although the first certain identification of a uranium mineral in rock other than pegmatite in Arizona was about 1913 (Gregory, 1917), no uranium ore was mined until 1942. From then until the end of 1944 about 11,600 tons of uranium-vanadium ore was mined from deposits in Apache County primarily for vanadium, which was in great demand during the early part of World War II. The demand for vanadium diminished in 1944, and there was a full in mining until 1948 when the Atomic Energy Commission established a guaranteed price schedule for uranium ore with additional benefits and bonuses. These prices stimulated exploration and mine development and resulted in an established uranium mining industry. By the end of 1966 ore had been produced from a few hundred mines in Arizona. The production of ore is summarized in Table 23.

### Table 23—Uranium Ore Production in Arizona, 1942-66

<table>
<thead>
<tr>
<th>Year</th>
<th>Ore (short tons)</th>
<th>Value *</th>
<th>Year</th>
<th>Ore (short tons)</th>
<th>Value *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1942-44</td>
<td>11,400</td>
<td>$58,000</td>
<td>1961</td>
<td>228,200</td>
<td>$4,965,000</td>
</tr>
<tr>
<td>1944-45</td>
<td>215,500</td>
<td>7,167,000</td>
<td>1962</td>
<td>143,900</td>
<td>3,047,000</td>
</tr>
<tr>
<td>1945-46</td>
<td>146,400</td>
<td>4,015,000</td>
<td>1963</td>
<td>150,300</td>
<td>4,844,000</td>
</tr>
<tr>
<td>1946-47</td>
<td>147,100</td>
<td>4,923,000</td>
<td>1964</td>
<td>107,300</td>
<td>3,253,000</td>
</tr>
<tr>
<td>1947-48</td>
<td>291,300</td>
<td>4,503,000</td>
<td>1965</td>
<td>117,900</td>
<td>3,918,000</td>
</tr>
<tr>
<td>1948-49</td>
<td>277,500</td>
<td>5,355,000</td>
<td>1966</td>
<td>64,200</td>
<td>1,978,000</td>
</tr>
<tr>
<td>1949-50</td>
<td>307,100</td>
<td>6,805,000</td>
<td>1950</td>
<td>243,300</td>
<td>6,197,000</td>
</tr>
<tr>
<td>1950-51</td>
<td>277,400</td>
<td>6,372,000</td>
<td>1951</td>
<td>283,100</td>
<td>6,219,000</td>
</tr>
<tr>
<td>1951-52</td>
<td>283,700</td>
<td>6,219,000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Data furnished by Grand Junction Office, U.S. Atomic Energy Commission, except as noted.

Production reached a peak of 303,000 tons of ore in 1957 and declined irregularly thereafter. This decline was a result of depletion of easily discovered near-surface deposits during a period when announcements of future changes in price schedule diminished the incentive for prospecting. Among the changes in pricing were the termination in 1960 of a bonus for initial production of uranium ore, and a shift in 1962 to a mill concentrate pricing basis. At that time production was limited to an annual allotment for each mine. Also, in 1962, a supplemental program for domestic uranium procurement for the period January 1, 1961, to December 31, 1970, was announced. This provided for deferring delivery of some concentrate contracted for delivery before December 1967 and purchase by the Commission in 1968 and 1970 of a quantity of concentrate equal in amount to the pre-1967 quantity on which delivery was deferred. The price for this additional amount is based on allowed costs not to exceed $6.70 per pound of U₃O₈ in concentrate. After 1970, it is anticipated that most sales will be to a commercial market. In October 1967 it was announced that commercial buyers had contracted for 46,500 tons of U₃O₈, 15 delivered by the end of 1977. Thus, some of the causes of decline in national production appear to be the same.

### Deposits in Arizona

Uranium deposits in Arizona occur in rocks having a wide range in age and lithologic type. The deposits are of two general types, peneconcordant and veins, and are described below.

The most abundant and most generally productive are the peneconcordant deposits which are mainly in sandstone and conglomerate of continental origin. They consist of masses of rock impregnated with uranium minerals. Some of the mineralized rock is in lenticular layers and is concordant with the bedding. One type of mineralized rock elongate podlike masses which locally transect bedding. The deposits are generally elongate, tend to occur in clusters, and contain from less than a ton to many hundreds of thousands of tons of ore. The uranium content ranges from trace amounts to several percent, but the average grade of ore mined has been about 0.29 percent U₃O₈.

The mineral assemblages range from fairly complex to fairly simple depending on the relative contents of uranium and vanadium, the relative abundance of copper in some deposits, and the degree of oxidation. In the vanadiferous uranium deposits the ratio of V₂O₅ to U₃O₈ ranges from 0.1 to about 5:1. Although copper is present in some deposits it is not an important constituent.

Below the zone of oxidation, the minerals in the vanadiferous deposits are principally uraninite, coffinite, montroseite, and micaceous vanadium silicates; in the nonvanadiferous deposits, uraninite is the principal ore mineral. Copper sulfides occur in deposits where much copper is present. Pyrite is generally present, and galena and sphalerite, occur sparsely in some deposits.

In the oxidized zone near the surface the minerals of the vanadiferous deposits are mainly the uranyl vanadates—carnotite and tyuyamunite—and a variety of vanadium minerals. The minerals of the nonvanadiferous deposits include a wide variety of uraninite—compounds of which boltwoodite (hydroxyl potassium uranyl silicate), uuranohedrites (hydroxyl barium uranyl phosphates), and metatitanite are most common. The mineralogy of the deposits is described more fully by Austin (1964), Finch (1959), and Weeks, Coleman, and Thompson (1959).

All but a few of the peneconcordant deposits are in the Colorado Plateau province (fig. 4, p. 38), principally in rocks of Mesozoic age. About 53 percent of Arizona's production has come from deposits in the Chinle Formation of Triassic age, about 28 percent from the Morrison Formation of Jurassic age, and the remaining 19 percent has come from various other units and veins.

Deposits in the Chinle Formation are between the base and about 150 feet above the base. The larger and many smaller deposits are in discontinuous elongated masses of sandstone in the Shinarump Member that filled ancient stream channels cut into the underlying Moenkopi Formation (Withk and Thaden, 1963). Many small- and medium-sized deposits are in lenticular channel-filling sandstone in the lower part of the Petrified Forest Member (Chenoweth, in Akers and others, 1962).

The deposits are concentrated largely in two main areas, one in Monument Valley and the other near Cameron in the valley of the
Little Colorado River, but some are scattered along the outcrops of the Chiricahua Formation from northeastern Mohave County (No. 11, fig. 43) to southeastern Apache County (No. 8, fig. 43). In the Monument Valley area, all the deposits, including the two largest in the Chiricahua, the Monument No. 2 (No. 3, fig. 43), and the Moonlight (No. 4), are in the Shinarump Member as are other smaller deposits. They are grouped in a poorly defined northwesterly trending belt near the northeast pinchout of the member (Finch, 1960; Johnson and Thor-darson, 1966). In the Cameron area (No. 9, fig. 43) numerous small and medium-sized deposits are in the Petrified Forest and Shinarump Members (Chenoweth, 1963, and others, 1962).

The deposits in the Monument Valley area are vanadiumiferous, the ratio of $V_2O_5$ to $U_3O_8$ ranging up to 4.6 to 1 (Johnson and Thor-darson, 1966, p. 1125) whereas in the Cameron area vanadium is distinctly subordinate to uranium (Austin, 1964).

All the deposits of any consequence in the Morrison Formation are in the Salt Wash Sandstone Member. This member is present in the northeastern corner of the State in the vicinity of the Carrizo and Lukachukai Mountains (Strobel, 1956), and on the northeast and east sides of Black Mesa. It consists of lenticular lenses of sandstone inter-bedded with mudstone (Craig and others, 1955). In the vicinity of the Carrizo Mountains sandstone is dominant (Chenoweth, 1955, 1967). Nearly all the deposits in the Morrison are in the Carrizo Mountains area. Most of these fall within an ill-defined north-south belt about 5 miles wide, which extends from the northwestern edge of the Carrizo area (No. 2, fig. 43) to the Lukachukai Mountains (No. 1, fig. 43). A few are scattered on the northeast slope of the mountains, and along the east boundary of the State. Two small deposits (No. 5, fig. 43) are on the northeast slope of Black Mesa. At least 85 percent of the ore mined from deposits in the Morrison has come from the Lukachukai Mountains.

Deposits in the Lukachukai Mountains area are in the middle half of the Salt Wash Member, whereas those farther north are in the lower part.

All the Morrison deposits are vanadiumiferous. Although the $V_2O_5$:$U_3O_8$ ratio ranges from about 1:1 to 10:1, the ratio in ore shipped has averaged close to 4.5:1.

Peneconcordant deposits are relatively sparse in rocks of other ages in Arizona. Only a few in Cretaceous rocks on the northeast part of Black Mesa (No. 6, fig. 43) and the Uranium Aire deposit (No. 18, fig. 43) in Tertiary rocks have been appreciably productive. Deposits in Cretaceous rocks are in fluvial sandstone interbedded with carbonaceous siltstone in the upper part of the lower member of the Toreva Formation (Clinton and Carithers, 1956, p. 447-448). The deposits are roughly tabular bodies that contain a few hundred to a few thousand tons of vanadiumiferous uranium ore. Carnotite and tyuyamunite are the principal uranium minerals.

The Uranium Aire deposit consists of two beds of mineralized carbonaceous mudstone enclosed in beds of partly silicified limestone and mudstone that accumulated in a lake. These beds of probable late Tertiary age are part of a sequence that also includes fluvialite sandstone and conglomerate and some lava flows (Reyner, Ashwill, and Robison, 1966). The mineralized beds are about 85 feet apart stratify.
The rocks in the structure are fractured, disoriented, and displaced from their normal stratigraphic position. Blocks of Coconino Sandstone are displaced downward at least 275 feet. Much of the ore is at the stratigraphic position of the upper, cliff-forming part of the Supai Formation. The larger part of the ore is in the arcuate body generally concordant with the north wall of the collapse, where it is partly in fractured rocks of the pipe wall and partly in adjoining pipe-filling material. A smaller part of the ore is in more poorly defined bodies in the ring-fracture zone along the southeast wall and in sandstone in the interior of the pipe.

Uraninite is the principal ore mineral. It is accompanied by pyrite and other sulfide and sulfosalt minerals that contain copper, silver, lead, zinc, cobalt, nickel, and molybdenum and have been a source of some copper and silver.

The Hack's Canyon mine (No. 12, fig. 43) (Granger and Raup, 1962) and the Ridenour mine (No. 13, fig. 43) (Miller, 1954) are deposits similar to the Orphan but smaller, and some uranium ore has been mined from them. Other similar deposits that contain uranium but have not been mined for it are the Copper Mountain mine, which was a source of high-grade copper ore (King and Henderson, 1953; Hill, 1913), and the Copper House prospect (No. 14, fig. 43) (Meehan, R. J., 1953). At the River View deposit in the Cameron area (No. 9, fig. 43) uranium has been mined from brecciated sandstone of the Shinarump Member of the Chinle Formation which collapsed downward to fill a pipe-like structure at the stratigraphic position of the underlying Moenkopi Formation (Chenoweth and Blakemore, 1961, p. 112).

Uranium is concentrated locally in rocks which fill some diatremes among the Hopi Buttes in Navajo County (Shoemaker, Roach, and Byers, 1957). At the Morale claim (No. 7, fig. 43), from which some ore has been mined, uranium in unidentified form occurs in laminated siltstone and tuff where they are flexed over slumped blocks of slightly older tuff near the southeast wall of the diatreme. The deposit is thought to be related to hot spring circulation late in the evolution of the diatreme and hence is grouped with the veins.

Vein deposits in the Basin and Range province and marginal areas of the Colorado Plateau province are in a variety of rocks that range in age from Precambrian to Tertiary. The most abundant and productive of these are in Gila County in the Dripping Spring Quartzite of Precambrian age.

Almost all the deposits in the Dripping Spring Quartzite are in the Sierra Ancha region north of the Salt River (No. 22, fig. 43). A few are in the Mescal Mountains (No. 23). Individual deposits have been the source of a few tons to several thousand tons of ore. Collectively about 25,000 tons of ore have been produced from them. Granger and Raup (1959) have studied the deposits and the following summary is drawn from their descriptions.

All the deposits are in thinly stratified arenaceous siltstone in an interval between 45 and 150 feet above the base of the upper member of the Dripping Spring Quartzite. The Dripping Spring Quartzite and underlying formations are intruded by sills and dikes of diabase. All the deposits are less than one-half mile from diabase and some are in rock bordering diabase.

Most of the deposits are vein-like zones generally less than 5 feet wide, a few to 15 feet high, and a few tens of feet to a few hundred feet in length. Some are manto shaped, nearly concordant with the bedding and some are combinations of veins and manto shapes. Many deposits follow directions which are defined near the surface by limonite-filled fractures and joints that trend either about N. 70° W. or about N. 25° E. In some deposits the exposed fracture fades out with depth, but the ore body continues along the same trend; in others the fracture diverges from the trend of the ore body.

Uraninite has been identified in 15 deposits near diabase. In other deposits the uranium minerals are either secondary minerals or are unidentified. Pyrite, marcasite, chalcopyrite, and less abundant galena and sphalerite occur in nearly all deposits. Pyrrhotite and molybdenite are present in a few near diabase.

Other small vein deposits are widely distributed in and adjoining the Basin and Range province. The ore produced from about a dozen deposits totals less than 1,000 tons. These deposits are identified and their main
Table 24.—Miscellaneous uraniferous vein deposits in and adjoining the Basin and Range province, Arizona

<table>
<thead>
<tr>
<th>Locality No. in fig. 43</th>
<th>County and name of deposit</th>
<th>Characteristics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>Star No. 1</td>
<td>Urenium-bearing vein at margin of mafic dike in granite of Precambrian age.</td>
<td>W. L. Chenoweth, oral communication, 1966.</td>
</tr>
<tr>
<td>19</td>
<td>Horsehoe group</td>
<td>Mineralized gouge in E-W to N-S trending, near-vertical fault cutting granite; uranium mineral not identified.</td>
<td>Robinson, 1953b.</td>
</tr>
<tr>
<td>19</td>
<td>Lucky Find group</td>
<td>Mafic dike in Precambrian granite is brecciated and mineralized at intersection with fault. Autunite present.</td>
<td>Robinson, 1954a.</td>
</tr>
<tr>
<td>15</td>
<td>Manley and Bickle group</td>
<td>Mineralized shear zone at intersection of N-E and N-S trending shears in Precambrian granite contains fluorite, calcite, and yellow uranium mineral.</td>
<td>Ashwill, 1955.</td>
</tr>
<tr>
<td>24</td>
<td>Linde Lee claim</td>
<td>Steeply dipping veins in arkose near contact with granite rock contain hematite accompanied by torbernite and gummite.</td>
<td>Robinson, 1955a.</td>
</tr>
<tr>
<td>16</td>
<td>Hillside mine</td>
<td>Iron ore vein (lead-ore) and lead in at least of Yavapai Group (Pennsylvanian) locally contains pitchblende, fluorite, and secondary uranium minerals.</td>
<td>Anderson, Scholz, and Strobell, 1955; Wright, 1956.</td>
</tr>
</tbody>
</table>

Resources

As of January 1, 1967, the U.S. Atomic Energy Commission estimated that uranium reserves in Arizona, minable under present and immediately prospective conditions, were about 125,000 tons of ore that averaged at least 0.4 percent U. Nearly all this reserve is in the Colorado Plateaus province, mainly in the Chinle and Morrison Formations, and in the Orphan mine. This amount is only enough to support mining for about two years at the 1966 rate of mining. Reserves have diminished steadily from nearly 1.2 million tons at the beginning of 1960. The decrease is a result of mine depletion accompanied by lack of incentive for exploration most of the time since 1960. This trend could be reversed as the market for uranium becomes more favorable, for the reserves represent only a part of the resource potential. The undiscovered portion of this potential is estimated to be at least two times as large as the portion already discovered.

The undiscovered resources probably are mostly in the Chinle and Morrison Formations and in collapse breccia pipes like that at the Orphan mine. The Shinarump Member and the lower part of the Petrified Forest Member of the Chinle Formation underlie a large area in northeast Arizona on the northeast side of the Little Colorado River. The most favorable places to explore for deposits are probably near pinchouts of the Shinarump Member such as those postulated by Stewart, Poole, and Wilson (1957, fig. 23). Concealed deposits may also be present in unexplored parts of areas underlain by the Morrison Formation in the northwest Carrizo (No. 2) and the Lukachukai Mountains areas (No. 1), and in rocks of Cretaceous age in the Black Mesa area (No. 6).

The known mineralized breccia pipes, such as the Orphan, have all been exposed by erosion. Other similar but unexplored pipes may be present in the Kaibab and Coconino Plateaus.

Deposits in the Chinle and in breccia pipes will be difficult and costly to find. Throughout much of the area where the lower part of the Chinle is present it is covered by 2,000 to 4,000 feet of younger rocks. The breccia pipes are relatively small targets a few hundred to 1,000 feet in diameter. Conditions would have to be at least as favorable for exploration as those in the mid-1950's to stimulate search for these deposits.

The tonnage of known marginal resources is about three times that of reserves. Part of these reserves are in deposits that were minable when incentive prices and bonuses were in effect, but are not mineable thereafter. Examples are some smaller scattered peneconcordant deposits in var-

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ous formations and vein deposits in the Dripping Spring Quartzite.
Part consists of rock too lean in uranium to have qualified for purchase
under the price schedules in effect up to 1962. Some of this low-grade
material adjoins ore in many deposits and an appreciable amount is
in tailings and mineralized rock at the Hillside mine (No. 16, fig. 43).
Some of these known marginal resources could be exploited if the
price for uranium equalized or exceeded the maximum of the late 1950's,
and additional marginal resources probably adjoin undiscovered deposits
of ore grade.

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VANADIUM
(By R. P. Fischer, U.S. Geological Survey, Denver, Colo.)

INTRODUCTION

The consumption of vanadium in the United States has increased appreciably in recent years; it averaged slightly less than 2,000 short tons a year during the 1950's, was 2,015 tons in 1961, and 5,481 tons in 1966, according to figures published by the U.S. Bureau of Mines. About 80 percent of the vanadium consumed has gone into engineering, structural, and tool steels, where it is used as an alloy to control grain size, impart toughness, and inhibit fatigue. The other principal domestic uses have been in nonferrous alloys and chemicals.

Because most of the vanadium-bearing ores mined in Arizona have been shipped to mills outside of the State and milled with ores from other sources, an exact figure of the vanadium recovered from Arizona ores is not available but it probably amounts to nearly 35 million pounds V₂O₅ (nearly 10,000 short tons V) contained in concentrates. This represents a little more than one-tenth of the total domestic production of vanadium and about one-twentieth of the total world output. The vanadium recovered from ores mined in Arizona has a value of about $40 million.

The bulk of domestic supplies of vanadium, and nearly half of the world supply, has come from vanadium-uranium deposits in sandstone in western Colorado and the adjoining parts of Utah, Arizona, and New Mexico. Other principal sources include a deposit of vanadium-bearing asphaltite in Peru, vanadate minerals in the oxidized zones of base-metal deposits in Africa, and vanadium-bearing iron deposits in Europe and Africa. Vanadium has also been obtained as a minor byproduct of phosphate rock mined in Idaho. In 1967 mining operations began in Arkansas on a vanadium deposit in highly altered rock at the contact of an alkaline igneous intrusion; this deposit is unique geologically and has not been classified as to geologic type. In Arizona, only the sandstone and vanadate types of vanadium deposits are known.

SANDSTONE-TYPE DEPOSITS

Slightly more than 90 percent of Arizona vanadium output has come from vanadium-uranium deposits in sandstone in the northeastern part of the State. Some of these deposits were mined for vanadium alone during World War II, but the bulk of the vanadium has come as a coproduct with uranium during the 1960's and 1970's. The symbols shown in figure 44 represent groups of deposits and are taken from Finch (1967, pl. 1), who identifies the individual localities. These deposits have yielded ore averaging 1 percent or more V₂O₅. Similar deposits of uranium in sandstone in other parts of northern Arizona (fig. 43) [uranium map] have a vanadium content that is too low to make its recovery profitable.

The productive vanadium-uranium deposits are in the Morrison Formation of Jurassic age in the Carrizo Mountains (Stokes, 1961;
Dodd, 1956) and Chilichito areas and in the Chine Formation of Triassic age in the Monument Valley area (Witkind, 1936; Malan, 1968), Apache and Navajo Counties. The host rocks are lensiform beds of stream-deposited sandstone that contain rather abundant carbonized plant fossils. Primary ore minerals consist of oxides and silicates of vanadium and uranium; all of these except the vanadium silicates oxidize to a variety of secondary minerals. The ore minerals impregnate the sandstone and replace the plant fossils, forming tabular ore bodies that lie nearly parallel to the bedding of the sandstone. These bodies average a few feet thick and range from small masses only a few feet across, containing only a few tons of ore, to bodies several hundred feet across, containing thousands of tons of ore. Ore bodies tend to be clustered in small areas or groups, represented by the symbols shown in figure 44.

Developed reserves of vanadium-bearing ore in the Morrison and Chine Formations in northeastern Arizona contain only a few hundred short tons of recoverable vanadium, representing about a 3-year supply at the rate of mining in recent years. Potential resources in undiscovered deposits, however, possibly contain as much as a few thousand tons of vanadium, but these deposits will be increasingly costly to find and mine. The outlook for their discovery and mining will be influenced chiefly by economic conditions in the uranium-mining industry in the future.

**Vanadate-Type Deposits**

The vanadate type of deposit consists of lead, zinc, or copper vanadates that occur in the oxidized zones of veins containing base metals. Commonly these vanadate minerals are sparsely and irregularly scattered in the oxidized parts of these veins and form more mineral occurrences, though in places these minerals are concentrated in patches or bodies from which some material of commercial grade can be obtained by selective mining. Deposits of this type are common in areas of arid or semiarid climates in many parts of the world.

In Arizona, reported vanadate occurrences (Galbraith and Brennan, 1959) are even more abundant than the symbols shown in figure 44, which were selected to represent the general distribution in the southwestern half of the State. In fact, most of the symbols shown probably represent more occurrences of vanadate minerals; only three deposits in the State are reported to have been productive. The deposit at the Mammoth-St. Anthony mine, Mammoth district, Pinal County yielded about 255 million pounds of V₂O₅ in concentrates during the 1934-44 period of operation (Creasey, 1950, p. 67). According to Peterson (1950, p. 101), about 20 tons of ore containing 5,877 pounds of V₂O₅ was shipped from the Defiance mine, Globe district, Gila County. During World War II a small amount of vanadium ore was shipped from the C and B property, Dripping Springs district, Pinal County.

There are no published data on reserves of vanadate ore in Arizona. Although continued mining in the oxidized zones of base-metal deposits in the State might find some commercial bodies of vanadate minerals, it is unlikely that this type of deposit will yield significant supplies of vanadium.

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### Zirconium and Hafnium

(By Richard T. Moore, Arizona Bureau of Mines, Tucson, Ariz.)

**Introduction**

Zirconium is the 20th element in abundance in the earth's crust, being even more abundant than copper, zinc, lead, or mercury. However, although the element is widely distributed, it rarely occurs in deposits of commercial grade. Elemental zirconium, which was first prepared in 1824, exists in two forms, a white crystalline metal, and a bluish-black amorphous powder. It has a specific gravity of 6.5 and melts at 1,857° C (3,375° F.).

Hafnium, the 47th element in abundance in the earth's crust, was not discovered until 1922. It is a metal very similar to zirconium in its chemical conduct and always occurs in minor amounts with zirconium. It has a specific gravity of 13.3 and melts at about 1,700° C (3,092° F.).

Zirconium and hafnium, because of their marked chemical similarity, are extremely difficult to separate completely (Bentler, 1965, p. 425). It was not until 1924 that pure zirconium metal was prepared, and it has only been in recent years that methods have been devised to extract all of the hafnium from zirconium ores on other than a laboratory scale. Hence, until recently, very few uses had been developed for hafnium; probably its greatest use has been as an electron emitter in electron-tube cathodes.

For many years, zirconium has been used as a getter (a substance used to clean up residual gases in electronic vacuum tubes). This use, however, consumes a very small amount of the total production. With the advent of nuclear energy, the greatest demand for zirconium metal has been as a structural material in nuclear power plants. In
this application it has adequate strength characteristics, good corrosion resistance, and a very low absorption power for slow neutrons (Eilertson, 1965b, p. 1108), which is essential to the maintenance of a chain reaction.

The increased demand for high purity metal resulting from its nuclear applications prompted the construction, in 1950, of the first major plant in the world for the production of zirconium. This plant at Albany, Ore., utilizes the Kroll process wherein zirconium tetra-chloride is reduced with magnesium to zirconium metal. By 1957, six plants had been put into production in the United States to fill Atomic Energy Commission contracts for zirconium metal.

With the arrival of the nuclear-power age, an important new use was developed also for hafnium. Unlike zirconium, hafnium has a high absorption power for slow neutrons and, thus, is well suited for use as control rods in nuclear reactors. Most of the hafnium metal produced since 1956 has been used in this application.

Although zirconium and hafnium are found in small quantities in several minerals, only zircon (ZrSiO₄) and baddeleyite (ZrO₂) are currently considered as commercial sources, and of these, zircon is the more important.

Although zircon is of great importance as a source of zirconium metal, by far the greater quantity of the mineral is used in other applications. Since 1950, as much as 80 percent of the zircon consumed annually in the United States has gone into the production of refractories, ceramics, and abrasives and into the formulating of foundry sands. In this latter use, the high melting point and lower thermal expansion of zircon, relative to silica and olivine sands, make it of value in forming precision molds.

**Occurrence and Source of Supply**

Baddeleyite, the zirconium oxide, contains 96–99 percent zirconium oxide and up to 3 percent hafnium oxide. It occurs as an accessory mineral with magnetite, ilmenite, corundum, and columbium-tantalum and rare-earth minerals, in some alkalic rocks. It is a rather hard, resistant mineral, so is amenable to concentration in placer deposits derived from these rocks. Baddeleyite has been found in placer deposits in Brazil and Ceylon. The only reported occurrences in the United States are in Montana.

Zircon, the zirconium silicate, contains 67 percent zirconium oxide and up to 4 percent hafnium oxide. It is found as an accessory mineral in many granitic and related igneous rocks, and as a constituent of placer sands resulting from the erosion of such rocks. As an accessory mineral, it commonly occurs as small, well-formed crystals, sparingly disseminated throughout the rock. Zircon is found also in rather large crystalline masses in some pegmatite rocks.

The production of zircon in the United States is chiefly from the southeastern Atlantic states, principally Florida, although deposits of potential commercial importance are recognized in several of the Western States (Kauffman and Holt, 1965). The major portion of the zircon consumed in this country, however, is from foreign sources, and Australia supplies about 85 percent of the tonnage annually imported. In 1965, these imports totaled 58,873 short tons of zircon of which 57,744 came from Australia (Parker, 1966, table 2).

Virtually all of the zircon consumed in the United States is produced as a coproduct or byproduct during the processing of heavy-mineral beach sands for the recovery of rutile and ilmenite. The sand is usually mined with dredges and treated by conventional gravity methods, such as Humphrey spirals, and finally separated with electrostatic and electromagnetic separators into the various heavy-mineral fractions.

**Zircon in Arizona**

Zircon is found in minor amounts at many localities in Arizona, and black-sand placer deposits in the Kirkland (Copper Basin) district, Yavapai County, fig. 45, No. 1, are reported to contain the mineral in potentially commercial quantities (Galbraith and Brennan, 1959, p. 97). These placer deposits are in Holocene alluvial material made up largely of sand, clay, and boulders derived from granite in the nearby Sierra Prieta (Wilson, 1961, p. 40); undoubtedly the zircon was originally present in the granite as an accessory mineral. It is possible that concentrations of zircon exist in similar alluvial deposits elsewhere in the State and if the demand for zirconium should increase sufficiently, then such deposits could be exploited.

Areas considered favorable for placer concentrations because of the occurrence of zircon as an accessory mineral in adjacent granitic or metamorphic rocks are shown in figure 45 and listed below. These data were largely compiled from Galbraith and Brennan (1959, p. 97).

<table>
<thead>
<tr>
<th>Locality</th>
<th>Deposit or occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Kirkland district</td>
<td>Placer deposits</td>
</tr>
<tr>
<td>2. Bradshaw Mountains</td>
<td>Accessory mineral in Bradshaw Granite</td>
</tr>
<tr>
<td>3. Globe vicinity</td>
<td>Accessory mineral in Rain Granite</td>
</tr>
<tr>
<td>4.</td>
<td>Accessory mineral in Pinal Schist and</td>
</tr>
<tr>
<td></td>
<td>Madera Diomite</td>
</tr>
<tr>
<td>5. Clifton-Morenci area</td>
<td>Accessory mineral in granite</td>
</tr>
<tr>
<td>6. Santa Rita Mountains</td>
<td>Microscopic grains in light-colored</td>
</tr>
<tr>
<td>7. Tombstone district</td>
<td>intrusive rocks</td>
</tr>
<tr>
<td>8. Bisbee district</td>
<td>Accessory mineral in granite and Pinal</td>
</tr>
<tr>
<td>9. Patagonia Mountains</td>
<td>Schist</td>
</tr>
</tbody>
</table>

However, as long as zircon is recovered in sufficient quantities as a coproduct or byproduct in conjunction with other heavy-mineral production, there is little probability that the Arizona deposits will become economically attractive.

**Selected References**

EXPLANATION

○ Placer deposits

X Occurrence

(Numbers refer to localities listed in text)

Figure 45.—Zircon in Arizona.
NONMETALLIC MINERAL RESOURCES OTHER THAN FUELS

ALUNITE

(By S. B. Keith, Arizona Bureau of Mines, Tucson, Ariz.)

INTRODUCTION

Alunite is a hydrous sulfate of potassium and aluminum KAl₃(SO₄)₂(OH)₆. When pure it contains 11.4 percent potassium oxide (K₂O), 37 percent alumina (Al₂O₃), 38.6 percent sulfur trioxide (SO₃), and 13 percent combined water. Sodium (Na) may substitute for potassium in alunite in variable amounts and varieties containing more sodium than potassium are called natroalunite. Alunite crystallizes in rhombohedrons resembling cubes; however, identifiable crystals are rare, and the mineral generally occurs in compact earthy or claylike masses or in finely disseminated particles. Most alunite is white or some shade of gray, but also may be brown and pink. Alunite is insoluble in water or weak acid, but when calcined a partly soluble potash alum is formed, and, after heating to high temperatures it consists mainly of potassium sulfate and alumina. Alunite has been recognized in several places in Arizona, and occurrences probably are much more abundant than now known, because it is difficult to distinguish from kaolin and jasperite with which it is commonly associated.

Alunite is formed by the alteration of feldspathic rocks by relatively strong hydrothermal or supergene sulfuric acid water. Porphyritic volcanic rocks, such as rhyolite, trachyte, and andesite containing feldspar phenocrysts, are particularly susceptible to alunization. Alunite also is common in altered zones associated with sulfide deposits in porphyritic granitic rocks. Less commonly it occurs in veins and irregular masses.

Prior to World War I, almost all potassium salts used in fertilizer and in industry in the United States were imported from Germany. The disruption of this supply during the war caused a critical shortage of potash and led to an intense search for domestic sources. The massive vein deposits in the Marysville district of Utah were the only known alunite deposits that appeared to be of commercial interest, and these were mined and processed. The production, however, was relatively small and expensive, and when imports of lower priced potassium salts from Europe were resumed after the war the mining of the Marysville deposits ceased. Subsequently, the search for domestic potash sources led to the discovery and development of the larger and more economically minable saline deposits in the southwestern states. Early in World War II, imported bauxite supplies for aluminum were threatened by submarine action, and alunite was considered as a possible source of alumina. The Kalunite process (Fleischer, 1944) was developed, and alumina and potassium sulfate were produced experimentally from the alunite of the Marysville deposits. Since the war a few thousand tons of alunite for fertilizer was produced from the Marysville deposits. There has been no other alunite production in the United States.

Alunite is used in other countries for several purposes. Potash alum and potassium sulfate have been made from alunite in Italy and New South Wales, Australia, and used in agriculture and in the chemical industry. Alunite is a source of alumina now produced by one plant in the U.S.S.R., and the similar use of this mineral is being considered in Mexico.

ARIZONA OCCURRANCES

The only known sizable deposit of alunite in Arizona which might be of commercial interest is at Sugarloaf Butte, 5 miles west of Quartzsite, Yuma County (N. center, T. 4 N., R. 20 W.). Alunite was first identified in this deposit by the Arizona Bureau of Mines in 1929, and the deposit has been described by Heineman (1935) and Thoenen (1941). The alunite occurs in a complex network of branching irregular veins which cut schistose and porphyritic dacite, and to a lesser extent cut sericite schist. The veins range from a fraction of an inch to a foot or more in width. Some are nearly pure alunite, but many are contaminated with quartz and a few contain gypsum. The purer alunite is white, massive, fine grained, and porcelainlike in appearance. Analyses reported by Heineman and Thoenen are shown in table 25.

According to Thoenen (1941, p. 11), the total rock that averages 55 percent alunite in the Sugarloaf Butte deposit is approximately 256,000 tons. A preliminary estimate by L. S. Gardner (written commun., 1942), considered that the total rock within 20 feet of the surface averaged 3.5 percent alunite and contained nearly 10 million tons. Additional alunite probably occurs at greater depths, but no estimate of the total size of the deposit has been made. Neither the Thoenen nor Gardner estimate distinguished alunite from natroalunite, but available analyses indicate the deposit is natroalunite.

TABLE 25.—PERCENTAGE CONTENTS OF ALUNITE AND OTHER CONSTITUENTS IN VARIOUS SAMPLES OF THE SUGARLOAF BUTTE ALUNITE DEPOSIT, YUMA COUNTY, ARIZONA

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Grab 1</th>
<th>High-grade vein 2</th>
<th>Composite of alunite rock and vein 3</th>
<th>Vein and wall rock 4</th>
<th>Vein 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alunite</td>
<td>(1)</td>
<td>(1)</td>
<td>55.0</td>
<td>52.5</td>
<td>57.8</td>
</tr>
<tr>
<td>Insoluble</td>
<td>(1)</td>
<td>(1)</td>
<td>17.0</td>
<td>17.0</td>
<td>16.7</td>
</tr>
<tr>
<td>SiO₃</td>
<td>7.44</td>
<td>1.70</td>
<td>20.3</td>
<td>20.3</td>
<td>22.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>35.19</td>
<td>38.50</td>
<td>20.5</td>
<td>20.5</td>
<td>22.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.14</td>
<td>1.45</td>
<td>1.33</td>
<td>1.33</td>
<td>1.40</td>
</tr>
<tr>
<td>K₂O</td>
<td>9.70</td>
<td>5.13</td>
<td>3.33</td>
<td>3.33</td>
<td>3.50</td>
</tr>
<tr>
<td>SO₃</td>
<td>38.10</td>
<td>21.2</td>
<td>13.60</td>
<td>13.60</td>
<td>22.3</td>
</tr>
</tbody>
</table>

1 Heineman, 1935, p. 139.
2 Heineman, 1935, p. 139; Thoenen, 1941, p. 11.
3 Thoenen, 1941, p. 11.
4 No data.

(301)
Alumite was identified by Schrader (1914, 1915) in the wall rock of the Evening Star prospect of the Three R Mining group, 5 miles south of Patagonia, Santa Cruz County (SE. cor., T. 22 S., R. 15 E.). The aluminitized zones, consisting of pinkish alumite and quartz, resulted from the alteration of orthoclase feldspar in pegmatitic granite along the wall of a sulfide vein. The zone may be several feet wide and in places may contain as much as 30 percent alumite. Alumite also was noted in strongly pyritized zones in the same area. No analyses or estimates of tonnage have been made. Alumite has been identified also in small disseminated amounts in the altered wall rocks of many sulfide deposits in Arizona, and reports of this type of occurrence are increasing. However, such occurrences are more of mineralogic than economic interest.

OUTLOOK

The possibilities for mining alumite in Arizona has attracted little interest in recent years. The known deposits, principally at Sugarloaf Butte, are too small to serve as the raw material for an aluminum industry, and the value of the deposits for other uses is decreased by their low grade and high sodium content. Some possibility remains that large high-grade alumite deposits will be found in Arizona in the future. However, the prospects for such discoveries cannot be considered bright, because alumite tends to occur in rocks favorable for metallic mineral deposits, and most such rocks have been thoroughly prospected.

SELECTED REFERENCES


ASBESTOS

(By A. F. Shride, U.S. Geological Survey, Denver, Colo.)

INTRODUCTION

Asbestos is a term applied in commerce to naturally fibrous silicates that are amenable to mechanical separation into fine filaments, which have some of the useful characteristics of organic fibers and are noncombustible. The six asbestos minerals that generally enter industry, in order of quantities used, are the fibrous form of serpentine known as chrysotile and five minerals of the amphibole group: crocidolite, amosite, anthophyllite, tremolite, and actinolite. Tremolite asbestos has been reported in Arizona (Wilson, 1938, p. 93) but all production has been of chrysotile. During recent decades chrysotile has constituted 90-95 percent of world consumption; crocidolite and amosite make up all but a minute part of the remaining commerce. These use ratios reflect in part the relative abundances of the various minerals (Bowles, 1935, p. 18-63) and in part the considerable differences of the minerals in flexibility, tensile strength, resistance to chemical corrosion, resistance to heat, electrical conductance and other properties (Badollet, 1951) that affect specific utility or ease of manufacture.

Variation in one physical property permits different lots of a specific asbestos mineral to be used in diverse products. For instance, chrysotile that can be flexed repeatedly like a thread of silk, without breaking, is designated as soft asbestos and if long enough the fibrils can be processed into textiles; in contrast, chrysotile that is harsh, or resilient like a broomstraw when flexed, is unsuitable to textile use but may exhibit filtration characteristics—lacking in the soft fiber—that especially enhance its manufacture into asbestos-cement products. Asbestos, then, is not a single commodity but a group of physically similar commodities that are fabricated, depending on specific characteristics, into a wide spectrum of products, which we accept as commonplace without fully appreciating how essential asbestos is in modern living and technology (Bowles, 1959).

In preparation for market, asbestos fibers are separated from enclosing rock and included mineral impurities and classified—generally to exacting specifications—according to length (see Jenkins, 1960, for summary of mill technology and comparisons of grade classifications). The longest crude chrysotile fibers (hand-cobbled fibers more than .5-inch long—the Groups 1 and 2 of the widely used Canadian classification) or equivalents and the longest grades of milled chrysotile fibers (Canadian Group 3) are processed into yarn, tape, roving, and cloth, which are fabricated into such products as brake linings, clutch facings, gaskets and packings.

Manufacturing technology in the industry is constantly changing to keep pace with new demands. Recently, for instance, fiber felts and cloths have been laminated with resins to form high strength, heat resistant sheets and molded forms that are being used increasingly in aerospace devices. Low-iron chrysotile in the form of roving or paper is used as electrical cable insulation. The bulk of chrysotile is much shorter than one-eighth inch. The fibers just shorter than the textile grade (Canadian Groups 4-6) are used principally in asphalt-cement products, such as pipe, sheets, corrugated and flat boards, millboard, and shingles. They are also used in molded friction materials, asbestos paper for air-cell insulation, roof coatings, putties, and gasket materials; the shortest fibers (Groups 6-7) find similar uses and also are incorporated in asphalt products such as floor tile and in paints. Miscellaneous uses include caulking compounds, filtration aids for processing blood plasma, wines and other liquids, and special papers.

The longest fibers command the highest prices. In recent years Nos. 1 chrysotile crudes have generally sold for $1,400 to $1,600 per short ton; Group 3 fibers have sold in the range of $850 to $900, and Group 7 material is valued at $40 to $80 per ton. Since World War II demand for asbestos has become more universal; consequently world production increased fourfold in 20 years, from about 825,000 short tons in 1946 to 3,350,000 short tons in 1966. During the same interval Canada, the principal producing nation, increased production from 58,000 tons to 1,479,000 tons. Since 1963
the annual production from Russia has apparently exceeded that of Canada. Annual consumption of the United States, the principal asbestos fabricating nation, has about doubled since World War II. During the 1960’s the United States has annually used 700,000 to 800,000 short tons, or 25-30 percent of world supply. Through the 1950’s the United States produced 41,000 to 54,000 tons, or 6 to 7 percent of the asbestos it consumed. This was largely short chrysotile fiber from Vermont. As the newly developed resources of California, mainly very short fibers, were put on the market in the early 1960’s domestic production more than doubled, so that 126,000 tons, or 15 percent of U.S. needs, were produced in 1966. Canada, which produces only chrysotile, has furnished 90-95 percent of U.S. imports. Crocidolite and amosite are available only from overseas sources, mainly those in southern Africa (Bowles, 1959, p. 25-46).

Most chrysotile is mined from extensive stockworks of veins that occur in massive bodies of serpentinized peridotite. These deposits are amenable to large-scale mining methods, and thus define the economics of the principal asbestos mining industry. Secondary sources are the small deposits—of which the Arizona deposits are prime examples—that occur as thin tabular layers of serpentine in limestone and furnish fibers somewhat different than those in the peridotite hosts. To illustrate, in the 1950’s when annual production from the Hance deposits, Quebec was on the order of 1 million tons, only 500 to 800 tons of fiber were recovered as long staple crudes. Practically no crude fiber was saved from domestic deposits of the peridotite type. In the same interval, out of an annual production of 2,000 to 4,000 tons in Arizona, 500 to 700 tons were crude fibers; indeed, apparently less than half of Arizona production has been of subtextile lengths—that is of Group 4 equivalent or shorter fibers. Prior to 1953, when low-iron chrysotile became available in significant quantities from northern British Columbia, the Arizona deposits were the only sources of strategic electrical grade chrysotile in the Americas. Thus, Arizona chrysotile is quite a different commodity than the short chrysotile from Vermont and California, which it complements; it is only partly competitive in use with those sources, and it can supplement the several thousands of tons of long fibers that we now annually import.

History and Production

The American asbestos industry began in 1878 when the great deposits of Quebec were first mined. Chrysotile was recognized about that time in the Grand Canyon and in Gila County, in Arizona, but none was mined until 1903 when small amounts were packed by burro from the Hance deposits in the canyon. 11 miles east of the present village of Grand Canyon (see fig. 46, locality No. 2). Sporadic attempts, the last in 1921, to develop these and the similarly remote Bass deposits (locality No. 1) 30 miles downstream in the canyon resulted in the mining of only a few tons of asbestos. In 1913 exploitation of deposits in central Gila County was started at the present site of the mining camp of Chrysotile. This set off a rush, which lasted through World War I, to locate and develop deposits further northwest in the county. Such activity was extended to the eastern part of

Figure 46.—Asbestos in Arizona.

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**Legend**

- Principal area of deposits
- Deposit or group of deposits outside principal areas

<table>
<thead>
<tr>
<th>Number</th>
<th>Deposit/Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bass (in Grand Canyon)</td>
</tr>
<tr>
<td>2</td>
<td>Hance (in Grand Canyon)</td>
</tr>
<tr>
<td>3</td>
<td>Wilson Creek - Walnut Creek area</td>
</tr>
<tr>
<td>4</td>
<td>Sluice Creek</td>
</tr>
<tr>
<td>5</td>
<td>Rock House</td>
</tr>
<tr>
<td>6</td>
<td>American Ores (Asbestos Peak)</td>
</tr>
<tr>
<td>7</td>
<td>Regal</td>
</tr>
<tr>
<td>8</td>
<td>Grandview and Ladder</td>
</tr>
<tr>
<td>9</td>
<td>Pinego (Lucky Seven)</td>
</tr>
<tr>
<td>10</td>
<td>Chrysotile</td>
</tr>
<tr>
<td>11</td>
<td>Bear Canyon</td>
</tr>
</tbody>
</table>

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**Explanatory Note:**

- Deposits referred to in text and listed below
- The map shows the location of the asbestos-producing region in Arizona.