

Reports

Silver from Ur of Ancient Mesopotamia

Abstract. *Silver jewelry from the Royal Tombs of Ur, about 2500 B.C., compares favorably in purity with present-day sterling, and it also met specifications recorded in cuneiform literature of a later period for similar objects. The original chemical composition has been greatly modified by corrosion, calcification, and chlorination. The source and diffusion of various elements detected were traced to study the original composition.*

Silver hair rings and pins from Ur of ancient Mesopotamia have been studied primarily by spectrochemical techniques to gain knowledge about the alloying and purity of silver used for jewelry by the ancients and to see if some correlation could be made between their cuneiform notations on purity and our analytical results. The main course of our investigation turned out to be the study of what happens to silver when it is buried underground for long periods of time. The objects are part of a collection from the University Museum, University of Pennsylvania, excavated by the late Sir Leonard Woolley between 1923 and 1934 from the Royal Tombs of Ur. They are dated from the Early Dynastic Period III, about 2500 B.C.

Our limited knowledge of the metallurgy of silver in ancient times comes mostly from translations of cuneiform tablets (1), which contain information on methods of refining silver, the exchange values of silver and silver currency, and the classification of silver by use. Little is given about the source of the ores, but references are made to a distant mountain, possibly the Taurus located in modern Turkey. The two major uses of silver were for currency and industrial purposes such as the making of jewelry. Silver for currency was of a low standard, in contrast to that for industry. Government regula-

tions protected the purity for industry and listed specifications for the fraction of silver to non-silver in 1 shekel of weight. One frequently noted fraction was $\frac{7}{8}$; others were $\frac{9}{10}$, $\frac{1}{2}$, and $1\frac{1}{2}$.

The objects we studied are shown in Fig. 1. The hair rings (items 2 to 6) are silver wire, 3 to 6 mm ($\frac{1}{8}$ to $\frac{1}{4}$ inch) thick, made into simple coils about 2½ cm (1 inch) in diameter with one to ten turns. The two hairpins (items 1 and 7), about 12½ cm (5 inches) long, vary in design. One is a tapered shaft with a hole drilled through the large end, while the other is a slender, slightly tapered rod with a lapis lazuli ball for decoration at one end. All are in a rather poor state of preservation and not suited for exhibition; thus permission was granted to perform destructive analysis as needed during the process of investigation. Our problem is complex because the objects remained underground for over 4000 years, and the original chemical composition is greatly modified by corrosion from various weathering conditions, by partial calcification, and by chlorination of the silver. Silver, along with other original elements, has diffused outward while contaminating elements have diffused inward, with the result that little, if any, of the original composition is intact. Fortunately,

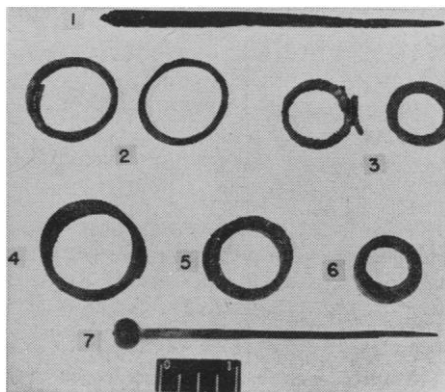


Fig. 1. Silver hair rings and pins from Ur.

stratifications can be seen in a cross-sectional cut, and a reasonable evaluation of the original composition can be made by separating the strata, analyzing them separately, and logically tracing the source and diffusion of each element detected. Spectrochemical techniques are adequate for this purpose.

Preliminary spectrochemical analysis of portions taken at random from several objects showed silver, as suspected, as the major constituent, with calcium and copper the next most prevalent along with about 20 other elements in lesser amounts. These results were used for making synthetic reference standards for more detailed analysis. The powdered form of pure silver metal, a 10-percent Cu-Ag alloy (coin silver), and chemically analyzed limestone were mixed together in different proportions. The limestone, a standard from the National Bureau of Standards, was calcined by us prior to addition to obtain better burning consistency in the carbon arc. Additional chemically analyzed and synthetic standards with AgCl and other silver compounds were used as the need arose.

The different strata were separated under magnification by cutting with a razor-sharp blade. In no case could a stratum be isolated without traces of others. Twenty-milligram weights of the separated materials were placed in specially designed graphite electrodes and "burned-to-completion" in a 14-amp direct-current arc. A dual grating Bausch and Lomb spectrograph was used for the analysis. Spectra of standards were recorded along with spectra of the unknown materials. Values for elements detected were obtained by visual comparisons of the densities of spectral lines of known amounts with corresponding lines in the material being analyzed. When reference standards were not available, estimates were based on published sensitivity values for spectral lines (2). Results are believed to be accurate within a factor of 2 for most elements determined.

Figure 2 is a schematic cross-sectional cut of a silver coil, based on the different strata observed and the conditions indicated by analytical results. The degree of preservation varies according to a number of factors, such as original composition, wire diameter, and especially to differences in weathering due to variations in the relationship of the object to its surroundings. The extent of most of these factors

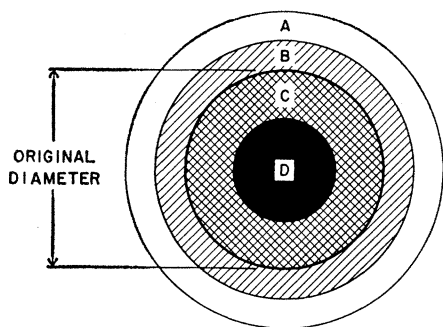


Fig. 2. Schematic cross-sectional cut of a silver coil based on the different strata observed and the conditions indicated by analytical results: *A*, Calcium carbonate redeposited from limestone by the reaction of atmospheric CO_2 and water. *B*, Calcium carbonate with AgCl and elements that have diffused out of the original silver. *C*, Silver chloride, metallic silver, and elements that are replacing the original silver. *D*, Remaining original silver.

is limited to speculation. Spectrochemical analysis of loose dirt from one ring indicates the presence of limestone, sand or clay, and alkali in the vicinity of the objects. Corrosion products from the silver show loss on ignition (750°C) to be as high as 30 percent because of water and other volatiles such as CO_2 from calcium carbonate. X-ray diffraction patterns identified AgCl as a major phase in several strata. AgCl was confirmed by dissolution in NH_4OH and reprecipitation in HNO_3 . An interpretation of the strata shown in Fig. 2 is as follows:

A (light yellow) is calcium carbon-

ate redeposited from limestone by the reaction of atmospheric CO_2 and water. Sand or clay is present in small amounts. Only traces of sodium were detected.

B (black to violet) is calcium carbonate with AgCl and elements (Au, As, Bi, Pb, Sn, and Zn) that have diffused outward.

C (violet) is AgCl and silver metal with calcium and other impurities (Mg, Si, Al, Fe, Ni, and others) that have diffused inward and replaced the original silver.

D (metallic) is the remaining silver.

The surfaces of the objects are not uniform and show areas that are black, grey-violet, and yellow. Since they are not uniformly yellow, indications are that the AgCl diffuses to the surface, for the most part, at a faster rate than the calcium carbonate is deposited. It can only be assumed that AgCl is formed by the metal gradually replacing the Na^+ ion in the NaCl that may be present, with the resultant alkali products being leached away. This is an unusual reaction that evidently requires a long period of time for completion.

Some conclusions may be drawn about the purity and composition of the original silver by correcting the analytical results of the remaining silver core (Fig. 2, *D*) for changes due to contamination and diffusion of the elements. To make allowances for differences in diffusion rates is beyond the scope of this study. Table 1 is a summary of results obtained and shows the composition of the purest silver found (almost 99 percent) and the concentration range for all objects. The evidence is that attempts were made to refine the silver as pure as practical and that copper was added to harden the metal and lower the melting point. The other elements are residual impurities. The compositional range is wide enough to suggest that the objects were made at different times with different starting batches.

Although spectrochemical analyses do not detect nonmetallic elements, it can be assumed that they were negligible. In purity the silver compares favorably with present-day sterling (92.5 percent) and, no doubt, could easily be worked into various objects. The objects predate most of our information about silver metallurgy of ancient Mesopotamia, which has been obtained from cuneiform tablets of the 3rd millennium B.C. Just what government controls

existed at the time the objects were made is not known; however, our study shows that by the Early Dynastic Period III the purity of silver for jewelry was high and well within requirements known from translations of a later period (3).

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References and Notes

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Gravity and Magnetic Anomalies of the Sierra Madera, Texas, "Dome"

Abstract. *A geophysical traverse across the Sierra Madera "Dome" indicates a negative gravity anomaly of $1\frac{1}{2}$ milligals over the zone of brecciation in the center and a residual positive anomaly of $\frac{1}{2}$ milligal associated with a positive magnetic anomaly of 25×10^{-5} oersted to the southeast of the zone of brecciation. Areal surveys are needed before any definite conclusions can be drawn concerning the origin of Sierra Madera. However, gravity and magnetic data can be extremely valuable in establishing criteria for classifying terrestrial and lunar features according to meteoritic and cryptovolcanic origin.*

The origin of the Sierra Madera "Dome" (in Pecos County, Texas), 275 m high, has been ascribed by various authors to the impact of a meteor (1). In August 1962, the gravity-magnetic traverse indicated on the geologic map (Fig. 1) was completed by a field crew from Texas Instruments. Figure 1 also shows the topographic, gravity, and magnetic profiles along the traverse and a schematic cross section of the surface geology. A negative gravity anomaly of about $1\frac{1}{2}$ milligals is centered over the zone of brecciation associated with the feature (Fig. 1, top). A local positive residual gravity anomaly of about $\frac{1}{2}$ milligal appears on this profile, coinciding with the east flank

Table 1. Chemical composition of silver jewelry from Ur. Results are given in percentage by total weight. ND, not detected. (Ca, Mg, Sr, and Si were present but are not reported as part of the original composition because the major source was traced to contamination from diffusion and other processes.)

Element	Purest object found (Fig. 1, item 3)	Concn. range for all objects
Ag	Major	Major
Cu	1.	1. - 5.
Pb	0.1	0.01 - 0.5
Au	0.05	0.02 - 0.1
Sn	ND	0.1*
Zn	ND	1.*
As	ND	ND - 0.2
Bi	0.1	0.02 - 0.2
Fe	0.01	0.01 - 0.05
Al	0.0003	0.0003 - 0.001
Ti	ND	ND - 0.005
Ni	0.002	0.001 - 0.02
Cr	ND	ND - 0.01
Mn	ND	ND - 0.01
B	ND	ND - 0.01
V	ND	ND - 0.02
Na	ND	ND - 0.05

* Present in one object only (Fig. 1, item 1).