CORROSION MINERALOGY OF AN 1800 SPANISH PIECE OF EIGHT

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ABSTRACT

Spanish colonial eight real silver coins, commonly called Pieces of Eight, were used throughout the Spanish-speaking world for hundreds of years. We undertook a detailed mineralogical, textural, and chemical investigation of an 1800 Carlos IIII eight real coin recovered from the wreck of the Spanish frigate *Santa Leocadia*, which sank on the rocky shore of Ecuador on November 16, 1800, with a loss of more than 140 lives and of 2,100,000 pesos of gold and silver coins. The coin is a typical eight real piece, composed of about 90% Ag and 10% Cu. It was buried in clastic sediments beneath the oxidized zone, such that it reacted with sulfur released by sulfate-reducing bacteria. Consequently, the coin has been totally encapsulated in a mixture of sand, gravel, and shell fragments cemented by metal sulfides. The residual coin consists of silver with small interspersed micrometric grains of copper. Reaction of the dissolved metal with the bacterially generated diagenetic sulfur in the intergranular fluids resulted in extensive cementation of the sediment particles by Ag and Cu sulfides. In the 1-mm zone immediately adjacent to the coin, Cu-bearing acanthite occurs as concentric layers with intervening zones of sand and clay. Beyond this zone, acanthite formed from Ag dissolved from the coin occurs as a more or less continuous interstitial cement with local small islands of covellite, CuS. Copper also occurs as films of Cu carbonate on quartz grains, as isolated grains of jalpaite Ag_3CuS_2, stromeyerite $AgCuS$, mckinstryite $(Ag,Cu)_2S$, and as atacamite $Cu_2Cl(OH)_3$, which rim and replace detrital carbonate grains.

Keywords: piece-of-eight, coin, silver, copper, acanthite, atacamite, corrosion, environmental mineralogy, archeology.

SOMMAIRE

Les pièces de monnaie de huit réals, que l'on appelle "pièces de huit", ont servi des centaines d'années de façon très répandue dans le territoire colonial espagnol. Nous avons entrepris une étude minéralogique, texturale, et chimique détaillée d'une pièce de huit réals datant de 1800 à l'effigie de Carlos IIII; elle a été découverte dans les restes du navire espagnol *Santa Leocadia*, qui a fait naufrage sur la côte accidentée de l'Equateur le 16 novembre, 1800, avec plus de 140 morts et une valeur de 2,100,000 pesos en pièces d'or et d'argent. Il s'agit d'une pièce de huit réals typique, contenant environ 90% Ag et 10% Cu. Elle a été enfouie dans des sédiments clastiques en dessous de la zone oxydée, de sorte qu'elle a subi les effets d'une réaction avec le soufre libéré par des bactéries capables de réduire le sulfate. Par conséquent, la pièce est totalement encapsulée dans un mélange de sable, gravoi, et fragments de coquillages, le tout cimenté par des sulfures des métaux. Le partie résiduelle de la pièce est faite d'argent parsemé de petits grains micrométriques de cuivre. Une réaction dans le fluide intergranulaire du métal dissous avec le soufre diagénétique généré par les bactéries a produit un ciment qui entoure les particules sédimentaires d'un revêtement de sulfures d'argent et de cuivre. Dans la zone de 1 mm immédiatement adjacente à ce qui reste de la pièce, l'acanthite cuprifère est disposée en couches concentriques, avec des intercalations de sable et d'argiles. Plus loin, l'acanthite formée à partir de l'argent libéré de la pièce forme une trame de ciment interstitiel plus ou moins continue avec, ici et là, des îlots de covellite, CuS. Le cuivre forme une

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pellicule de carbonate de cuivre sur les grains de quartz, et des grains isolés de jalpaïte Ag_3CuS_2, stromeyerite $AgCuS$, mckinstryite $(Ag,Cu)_2S$, et atacamite $Cu_2Cl(OH)_3$, qui recouvrent ou remplacent les grains détritiques de carbonate.

(Traduit par la Rédaction)

Mots-clés: pièce de huit réals, monnaie, argent, cuivre, acanthite, atacamite, corrosion, minéralogie environnementale, archéologie.

INTRODUCTION

The Spanish eight-real coin, commonly known as the "piece of eight", and as *peso fuertes,* was one of the most widely used coins throughout the world in the sixteenth, seventeenth, and eighteenth centuries. These coins were struck as early as about 1535 in Mexico City, and later in cities such as Potosí, Santo Domingo, Lima, Santa Fe de Bogota, and Santiago de Chile. The earliest of the coins were "cobs", irregularly shaped elongate to roughly circular pieces cut from silver–copper strips. Weight was the key, and each cob was trimmed until it was of the appropriate weight regardless of shape. Gold denominations were 8, 4, 2, and 1 escudos and silver denominations were 8, 4, 2, 1, and ½ reals; the weight of the 8-real coins was initially 27.468 g and was later adjusted to 27.064 g (Sedwick & Sedwick 1995). "Cobs" became more regular in shape in the early 1700s, and truly round milled coins first appeared from 1730 to 1750. The uniformity of the coins and their widespread use throughout the Spanish Empire resulted in their acceptance not only in Spanish America but also in the American colonies. Peterson (1969) noted that these "enjoyed the widest circulation of any coinage in history". When the United States began to mint its own coinage in 1792, it modeled the silver dollar on the eight-real coin, or Spanish milled dollar as it sometimes is called. Furthermore, the popularity of, and trust in, the Spanish piece of eight resulted in it remaining as legal tender in the United States until 1857. Where smaller-denomination coins were not available, pieces of eight were commonly cut into halves and quarters to serve as substitutes; the quarter or "two-bits" (of the total of eight) served as the basis for that common American slang term used for its quarter or 25-cent coin.

The broad usage of the pieces of eight resulted in their occasional dispersal and burial in a wide variety of geological environments. No doubt, many will never be recovered from their burial sites, and others have been totally destroyed by abrasion, weathering, and corrosion processes. This report on corrosion-induced mineralogy is based upon the study of an 1800 eight-real Carlos IIII coin minted in Lima, Peru and which was aboard the Spanish frigate *Santa Leocadia*, which sank off the rocky coast of Ecuador in 1800. Recovery of this coin along with other artifacts from the wreck began in the 1940s, largely by American servicemen stationed nearby. The exact date of recovery of this coin is not known, but it is apparent that the coin had lain in the sediments for a period of approximately 115 years.

THE SAMPLE AND ANALYTICAL METHODS

The coin was obtained from the Maritime Museum of the Florida Keys in 1992. The original dimensions of the coin were approximately 3.8 cm in diameter and about 2 mm in thickness, identical to those of the 1806 coin of the same denomination shown in Figure 1. The coin studied is believed, because of the identity of the other coins from the wreck, to have been among those produced at the Lima mint from 1788 until 1808. The coin was nominally 90 wt.% Ag and 10 wt.% Cu and weighed 27 g. Microscopic examination of the unaltered core of the coin in polished section reveals that it consists of a matrix of silver with dispersed elongate 1–5 μm grains of copper. The elongate nature of the copper inclusions likely resulted from rolling or pounding of the coin blank before it was cut and imprinted with the insignia on the two sides. Optical examination and electron-microprobe analyses reveal that the coin's composition is not uniform, but varies locally from about 4 to about 9 wt.% copper. When recovered, the coin was heavily encrusted with sand- to pebble-size sedimentary particles and was about 4.2 cm in diameter and 6 to 8 mm in thickness (Fig. 2). The degree of corrosion was so extensive that there were no features corresponding to the surface features. The encrusted coin was coated with cold-setting EPOFIX epoxy so that the coin and its encasing sediments could be held together during sectioning, mounting, polishing, and analysis. The sample was then cut and mounted as a circular section 3.2 cm in diameter and polished in a standard manner (Craig & Vaughan 1994); the sample was examined using standard reflected-light microscopic techniques. A photo-collage 91 cm (36 inches) long, copied in a much reduced form as Figure 3, was prepared to aid in the examination and analysis of the sample. Analysis was done using a Cameca SX–50 electron microprobe operated at 15 kV and 20 nA using synthetic sulfides and pure metals as standards. Analysis was carried out on selected spots and along traverses, with care taken to avoid the overlap of grains; in addition, X-ray mapping was carried out to determine the distributions and variations of selected chemical elements in the original coin, the envelope of corrosion phases, and the encapsulating sediments.

CORROSION-INDUCED MINERAL PHASES AND DISCUSSION

Coins have provided a rich archeological legacy, revealing information on commerce, the timing of

events, and routes of travel and trade. From a geochemical perspective, buried ancient coins may be viewed as geochemical indicators that provide insight into the environmental conditions to which the coins have been subjected since burial. Furthermore, the dissolution and reprecipitation of the metals from coins may be viewed as mini-ore-forming situations, that may provide insights into the formation of low-temperature ores. At the very least, the corrosion of coins, such as the one

described here, are long-term (at least 140 years in this case) experiments in the behavior of metals in the near-surface environment. The instability of free silver in the atmosphere or aqueous environments results in reaction of the silver with available anions to form oxide, sulfide or other corrosion-induced phases. The coin described here apparently was buried within the marine sediments sufficiently deeply that the environment was reducing and rich enough in sulfur to form layers of encapsulating sulfide minerals. The sulfur was no doubt generated by sulfate-reducing bacteria that occur in marine envi-

FIG. 1. An 1806 Carolus IIII coin, minted in Potosí, Bolivia, similar to the coin examined in this study. The "P" and "J" on the upper left part of the obverse side of the coin are assay marks indicative of the Potosí mint in modern Colombia. These mint marks were used from 1803 to 1824 on coins from the Potosí mint. The cypher on the lower left is over-inscribed "PTS", mint marks indicative of the Potosí mint from 1773 to 1825.
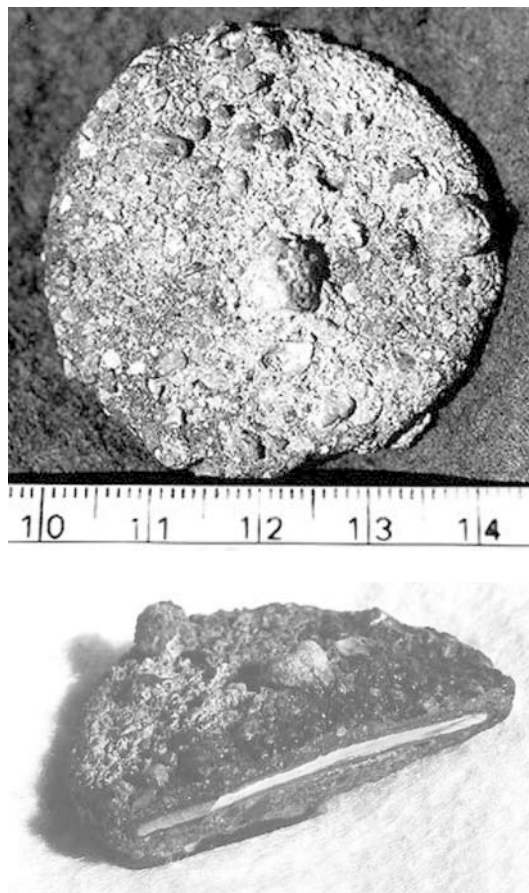

FIG. 2. (a) The coin described in this paper as it appeared when obtained. The remaining portion of the silver–copper coin, believed to be an 8-real piece minted in Lima, Peru in 1800, was completely encapsulated by an incrustation of sand, gravel, and shell fragments cemented together by silver and copper sulfides. The coin was coated with epoxy prior to cutting in order to preserve the textures of the encapsulating minerals. (b) After being cut, the remaining portion of the original coin is visible within the cemented mass of sediment.
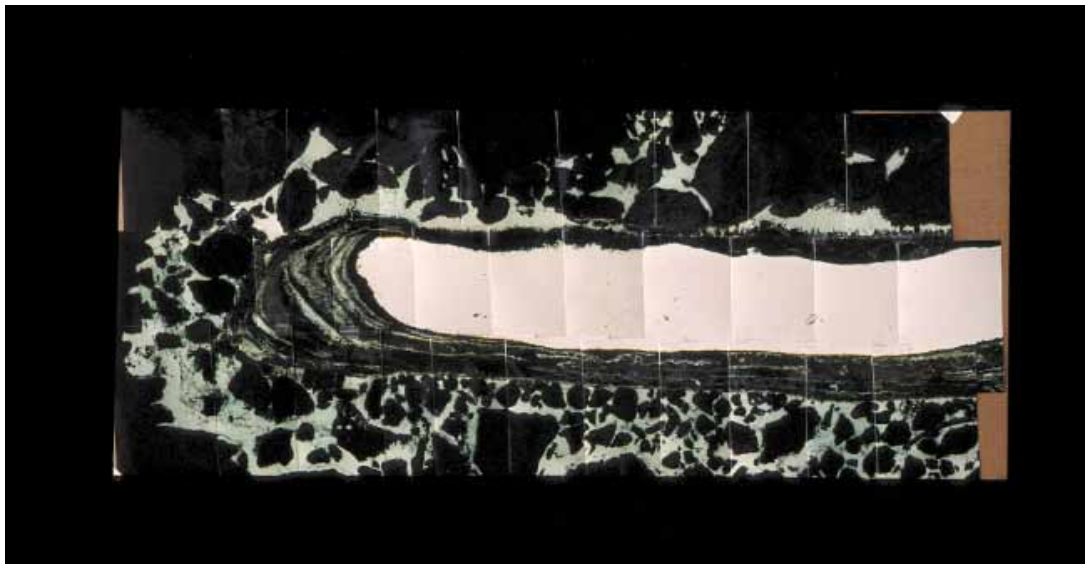
Fɪɢ. 3.   Reduction of a photo-collage 91 cm (36 inches) long constructed to provide an overall picture of the coin and its encapsulating phases and to aid in locating mineral phases during analysis. The metallic silver–copper core of the coin is approximately 1.5 mm in thickness. The light gray phase visible as concentric zones and as the cementing material between sand and fossil grains is acanthite (Ag$_2$S).

ronments around the world. The initial reaction probably took place in the temperature range 10–30°C and apparently resulted in the formation of copper-bearing acanthite (Ag$_2$S) as a thin surface-layer. Irregularities in this layer and pressures resulting from the volume increase created fractures at the acanthite–coin interface and allowed for the reaction of additional silver. As reaction continued with the sulfur (probably in the form of dissolved H$_2$S), the thickness of the acanthite increased to form the concentric layers visible in Figure 3. Seward & Barnes (1997) have pointed out the similarities of Ag and Cu and noted in particular the effectiveness of chloride as an important complexing agent for both elements. Undoubtedly, the high concentrations of chloride in the pore waters of the sediments served to dissolve Ag and Cu from the coin. The sulfur released by sulfate-reducing bacteria then reacted with the dissolved metals in close proximity to the coin, creating the encapsulating Ag and Cu sulfides. Acanthite is a common corrosion product on silver coins (North 1987), and the pattern displayed in this coin is nearly identical to the general pattern of coin corrosion described and illustrated by Scott (1991) in his Figure 65. The incorporation of grains of detrital sediment and even microfossil fragments indicates that dissolved Ag and Cu from the coin diffused through interstitial fluids only short distances (2 to 3 mm) before precipitating as the cement to bond the sediment and fossil fragments. The acanthite typically contains 1–2 wt.% Cu (Table 1), but locally

contains as much as 8 wt.%. Most of the acanthite occurs as anhedral polygranular aggregates, but some crystals possess terminations where growth into open voids was undisturbed.

The relative dominance of the silver over copper in the coin is reflected in the corresponding abundance of acanthite relative to copper sulfide (covellite, CuS) in secondary sulfide minerals. Covellite is present as small, commonly somewhat radially disposed masses of crystals that are up to 20 µm in length (Fig. 4). The covellite, which contains as much as 11 wt.% Ag (Table 1), displays normal color, bireflectance, and anisotropy of covellite when first viewed, but if left under normal reflected light illumination (halogen, 120-V bulb with a blue daylight filter), the mineral slowly bleaches to white. The nature of this photo-activity is otherwise unknown, but probably indicates that the high silver content of the phase has affected its stability. It is not known if the reaction results from the minor heating effect of the light beam or the energy of the light photons.

Reaction of the silver and copper with sulfur has also resulted in the formation of stromeyerite AgCuS, mckinstryite (Ag,Cu)$_2$S, and jalpaite Ag$_3$CuS$_2$ (Table 1). These minerals lie along the Cu$_2$S – Ag$_2$S join in the system Ag–Cu–S and probably represent, at best, very small realms of local equilibrium within the crystallizing mass of acanthite. In his study of the system Ag–Cu–S, Skinner (1966) suggested that each of these

TABLE 1. CHEMICAL COMPOSITION OF PHASES PRESENT
IN THE COIN AND PRODUCTS OF CORROSION

Cu	Ag	S	Cl	Total	Cu	Ag	S	Cl	Total
				Acanthite					
8.64	75.24	15.59	0.08	99.55	10.29	52.77	36.78	0.16	100.0
5.85	77.67	14.54	0.09	98.15	7.27	56.79	35.75	0.19	100.0
7.33	77.04	12.85	0.04	97.26	9.14	56.57	34.21	0.09	100.0
5.80	78.75	14.60	0.11	99.26	7.13	57.11	35.54	0.23	100.0
8.11	79.67	13.72	0.18	101.68	9.83	56.85	32.93	0.39	100.0
0.62	83.82	12.71	-	97.15	0.82	65.67	33.51	-	100.0
				Silver in Coin					
7.86	90.21	0.13	-	98.11	12.83	86.77	0.40		100.0
3.98	95.49	-	-	99.47	6.62	93.39	-	-	100.0
6.51	91.23	0.09	-	97.83	10.78	88.94	0.28	-	100.0
8.83	90.09	0.09	-	99.01	14.22	85.49	0.28	-	100.0
3.61	95.96	0.04	-	99.61	6.0	93.86	0.14	-	100.0
7.33	92.63	0.07	-	100.03	11.82	87.96	0.22	-	100.0
7.03	94.12	0.06	-	101.21	11.24	88.57	0.19	-	100.0
				Jalpaite					
14.52	71.23	14.88	-	100.63	16.88	48.80	34.51	-	100.0
13.47	71.45	13.97	-	98.89	16.18	50.57	33.25	-	100.0
14.01	72.04	13.88	-	99.93	16.69	50.54	32.77	-	100.0
13.31	71.60	13.81	-	98.72	16.06	50.91	33.03	-	100.0
13.73	71.43	14.96	-	100.12	16.07	49.24	34.69	-	100.0
13.16	71.33	14.56	-	99.05	15.67	50.00	34.33	-	100.0
12.94	72.84	15.31	-	101.09	15.02	49.79	35.20	-	100.0
12.12	73.43	14.40	-	99.95	14.44	51.55	34.01	-	100.0
				Mckinstryite					
23.73	58.89	16.52	-	99.14	26.03	38.05	35.92	-	100.0
27.41	53.40	17.96	0.15	98.92	28.93	33.21	37.57	0.29	100.0
				Stromeyerite					
34.26	44.56	19.54	0.02	99.38	34.31	26.88	38.79	0.03	100.0
34.98	44.32	20.13	0.01	99.44	34.58	25.81	39.44	0.18	100.0
				Atacamite					
55.19	-	-	16.09	96.5*					
57.71	-	-	16.52	98.5*					
56.47	-	-	16.73	98.8*					
				Covellite					
0.00	7.81	32.12	-	99.9					
57.47	10.54	31.99	-	100.0					

Results of electron-microprobe analyses expressed in wt.% on left, and recalculated
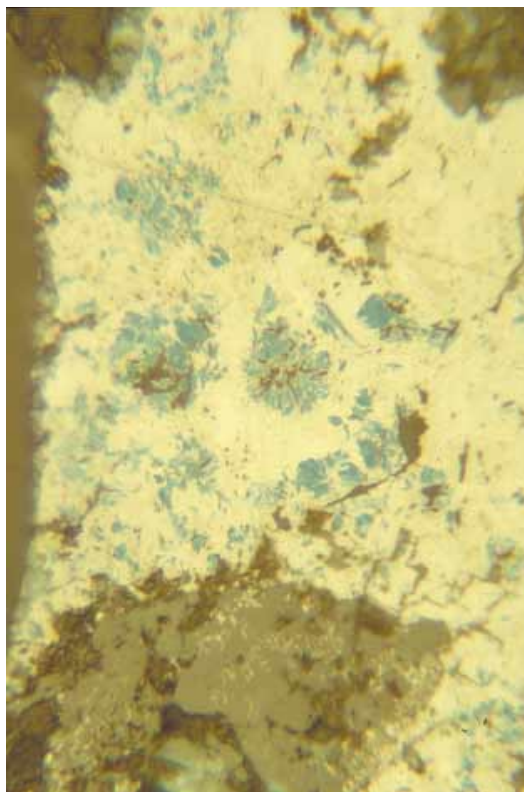in terms of atom % on right. * (OH) component calculated.

FIG. 4. Covellite, CuS, occurs as isolated, commonly somewhat radiating clusters of crystals within the acanthite. Height of the field of view is 0.6 mm.

minerals could exist stably with covellite or with silver, but that only jalpaite could stably coexist with acanthite. Given the low temperature of reaction (10–30°C), a sulfur flux that was probably changing, and possibly significant variations in the oxidation potential, a lack of overall equilibrium would not be surprising. The high Ag contents of the covellite and the high Cu contents of the acanthite further suggest that there may be significant metastability in the mineral assemblages. North & MacLeod (1987) noted that the similarity of some physical properties of copper and silver may lead to the formation of mixed sulfides, such as jalpaite, and this mineral was reported to have formed on some silver coins from the wreck site of the *H.M.S. Association*. The presence of characteristic copper green reflections along the margins of some quartz grains suggests the likely presence of some copper carbonate. Such coatings are extremely thin and irregular, but are seen locally while examining the sample in reflected light.

A copper-hydroxy-chloride, $Cu_2Cl(OH)_3$, equivalent to the composition of the four polymorphs atacamite, paratacamite, clinoatacamite, and botallackite, is distributed throughout the sample as small grains, where it has apparently formed through the replacement of calcite shell fragments, as shown in Figure 5. It has not been possible to ascertain which of these minerals is present. These minerals have been reported from diverse environments (Pollard *et al.* 1989, Hannington 1993) and atacamite and paratacamite may be stable minerals. Botallackite is much rarer, and its stability is questionable. Sharkey & Lewin (1971) reported that paratacamite "appears to be the thermodynamically stable phase at 100°C and higher … and atacamite may be more stable at room temperature". Woods & Garrels (1986) noted that "paratacamite is the usual product in acid solutions, whereas atacamite has been precipitated in the laboratory under more alkaline conditions". This would be consistent with Hannington's observation that atacamite was the most abundant of the three phases forming during the alteration of seafloor sulfide mounds.
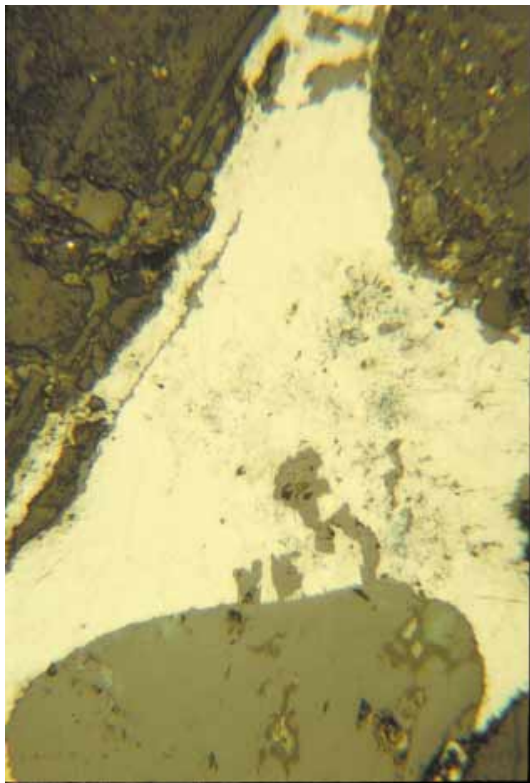
FIG. 5. Atacamite $Cu_2Cl(OH)_3$ occurs throughout the sample as a replacement, in whole or in part, of grains of calcium carbonate, as shown in this figure. Atacamite is the slightly lighter gray, somewhat oval phase visible near the bottom of the photo; the darker gray phase is calcite. The bright matrix is acanthite. Width of field of view: 0.6 mm.
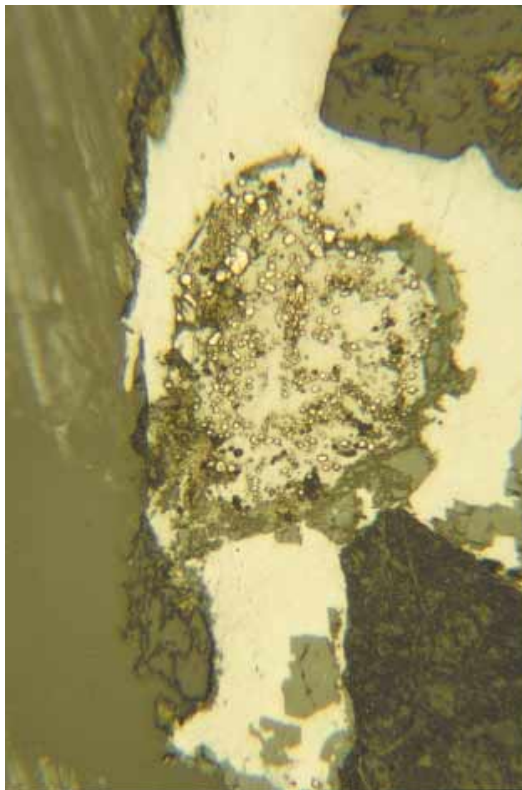

FIG. 6. Clusters of pyrite framboids are present in the acanthite (light colored). The darker phase is quartz. Width of field of view: 0.3 mm.

Furthermore, Garrels & Stine (1948) described the replacement of calcite by atacamite, similar to the situation illustrated in Figure 5. Accordingly, we herein refer to this phase as atacamite, but acknowledge the lack of definitive confirmation. Atacamite has been observed forming as a product of corrosion on copper-bearing artifacts (Lewin & Alexander 1968, MacLeod 1982, North & MacLeod 1987, Stoffyn-Egli *et al.* 1998).

Small amounts of pyrite have been observed as clusters of framboids (Fig. 6) and as thin rods, 5 μm long, within fragments of coral entrapped in the acanthite mass around the coin. This, of course, is not surprising given the amount of Fe available in sediments and the high activity of sulfur at the site.

The nature of the corrosion and the redistribution of elements that have reacted with the metals of the coin are well documented in the X-ray maps of Cu, Ag, S, and Cl (Figs. 7a, b). In each of these, higher brightness (more white) indicates greater concentration of the ele-

ments; because of significantly different concentrations of the elements, the brightness has been adjusted to maximize the display of each element separately. The image for Ag in the upper left of Figures 7a and 7b shows the greatest concentrations of silver in the remaining core of the coin. The slightly higher-intensity zones of Ag around some of the margins consist of Cu-free (hence slightly more Ag-rich) acanthite. The image for Cu at the upper right shows the concentrations of copper as inclusions in the coin but also shows the areas of Cu-bearing corrosion products (covellite, stromeyerite, mckinstryite, and jalpaite). The sulfur-distribution map in the lower left closely corresponds to the overall distribution of silver and copper because its presence in this sample is restricted to the sulfide minerals. The chlorine-distribution map corresponds closely with that for Cu because the only Cl-bearing mineral recognized is atacamite. In general, the atacamite occurs around the margin of the cemented portion of the samples, possibly because this part had the greatest exposure to the seawater-derived chloride.
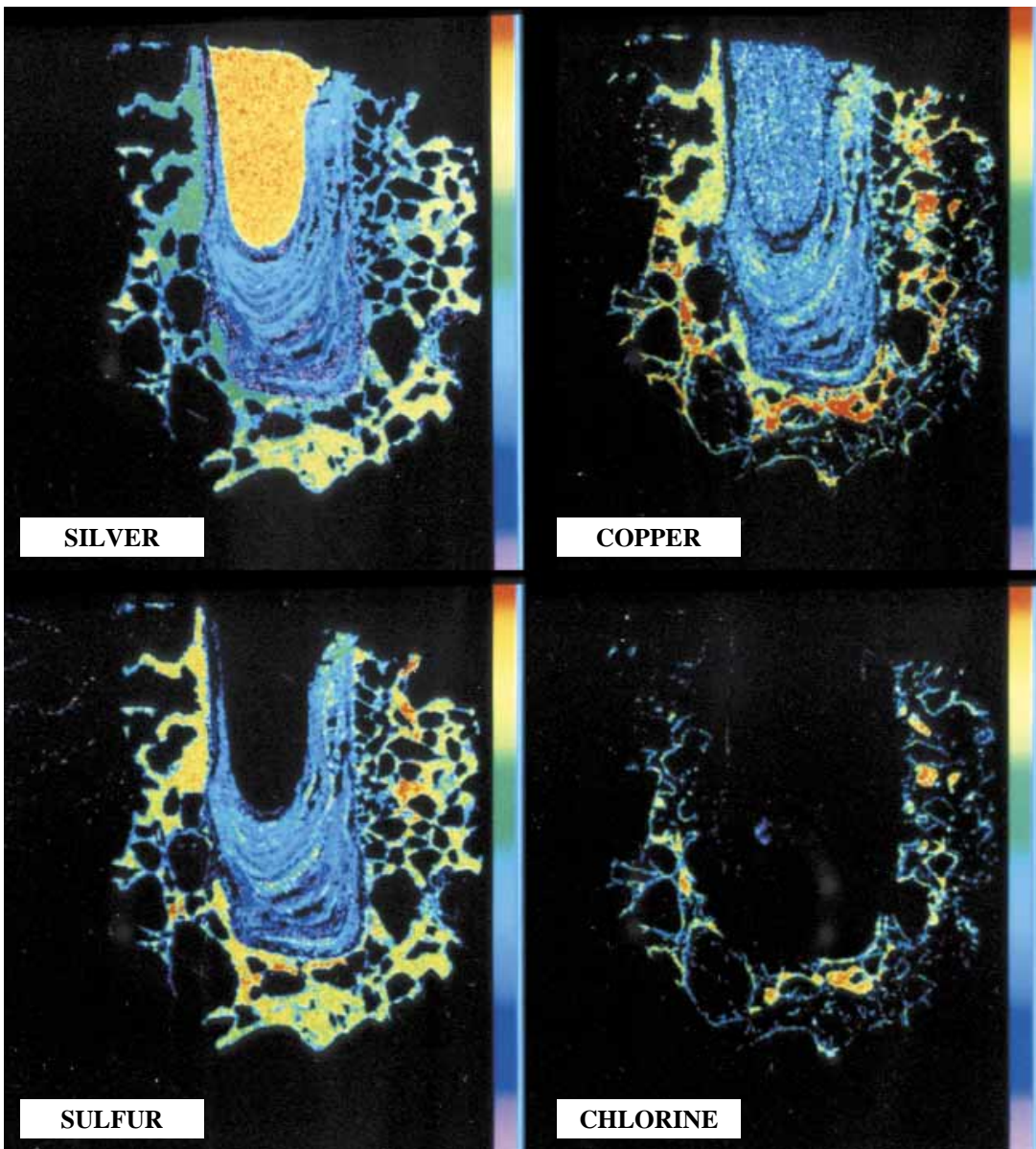
FIG. 7. Element-distribution maps showing the coin and the enclosing sediments. X-ray maps show the distribution of Ag, Cu, S, and Cl at the rim of the coin, and illustrate the concentric layers that typically develop as corrosion proceeds. The color bar is indicative of the concentration of the element; red is the most concentrated, followed by yellow, green, *etc*. The total length of the area shown is about 4 mm.

Chemical maps for Ag, Cu, S, and Cl as well as for Ca, Mg, Si, and Al were prepared (Fig. 8) for a central portion of the coin to better understand the distribution of secondary and diagenetic phases in the cemented coin-bearing mass. Detrital quartz is readily apparent as the brightest grains in the lower left-hand part of the figure; feldspar grains are present where both Si and Al (lower right) are present. The map for Ca shows the presence of fossil shell fragments (discrete grains) and the development of a rim of calcium carbonate cement
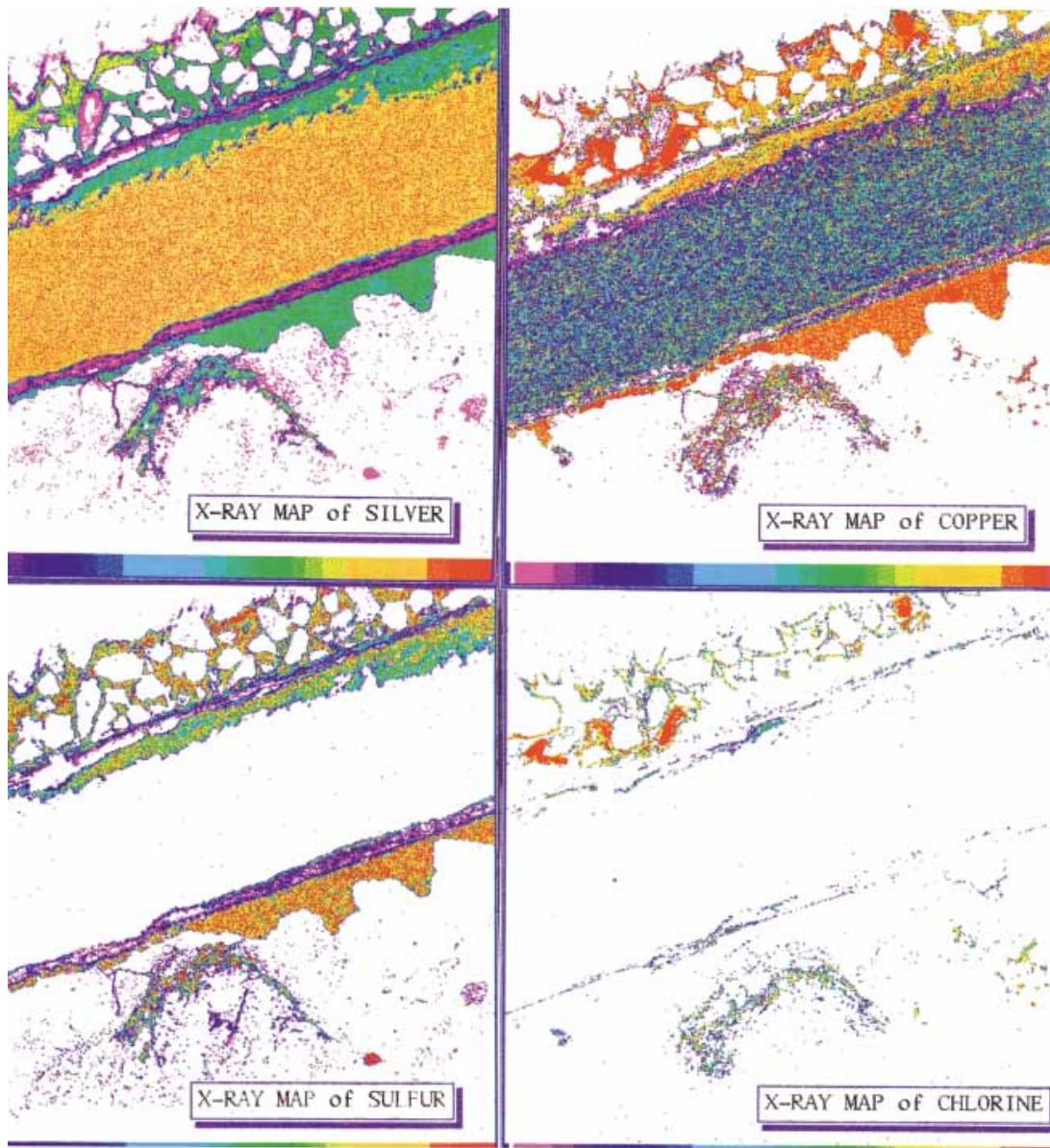
Fig. 8.   Element-distribution maps for the central portion of the coin illustrate the distribution of Ag, Cu, S, Cl, Si, Al, Ca and
      Mg. The unreacted coin contains the highest concentrations of silver; copper is enriched in some parts of the copper-bearing
      acanthite and in the copper hydroxy-chloride atacamite. The highest chlorine concentrations represent grains of atacamite.
      The color bar is indicative of the concentration of the element; red is the most concentrated, followed by yellow, green, *etc*.
      The width of the area shown in the maps is about 3.5 mm.

around the edge of many grains and along the margin of the coin. The map for Mg reveals that the rims of calcium carbonate consist of Mg-bearing calcite. Microscopic examination of the corroded coin revealed the presence of large numbers of needle-like crystals that grew from the sedimentary grains and extended into what were initially open voids between the grains (Fig. 9). That the needles (probably aragonite) are com-

X-RAY MAP of SILICON

X-RAY MAP of ALUMINUM

X-RAY MAP of CALCIUM

X-RAY MAP of MAGNESIUM
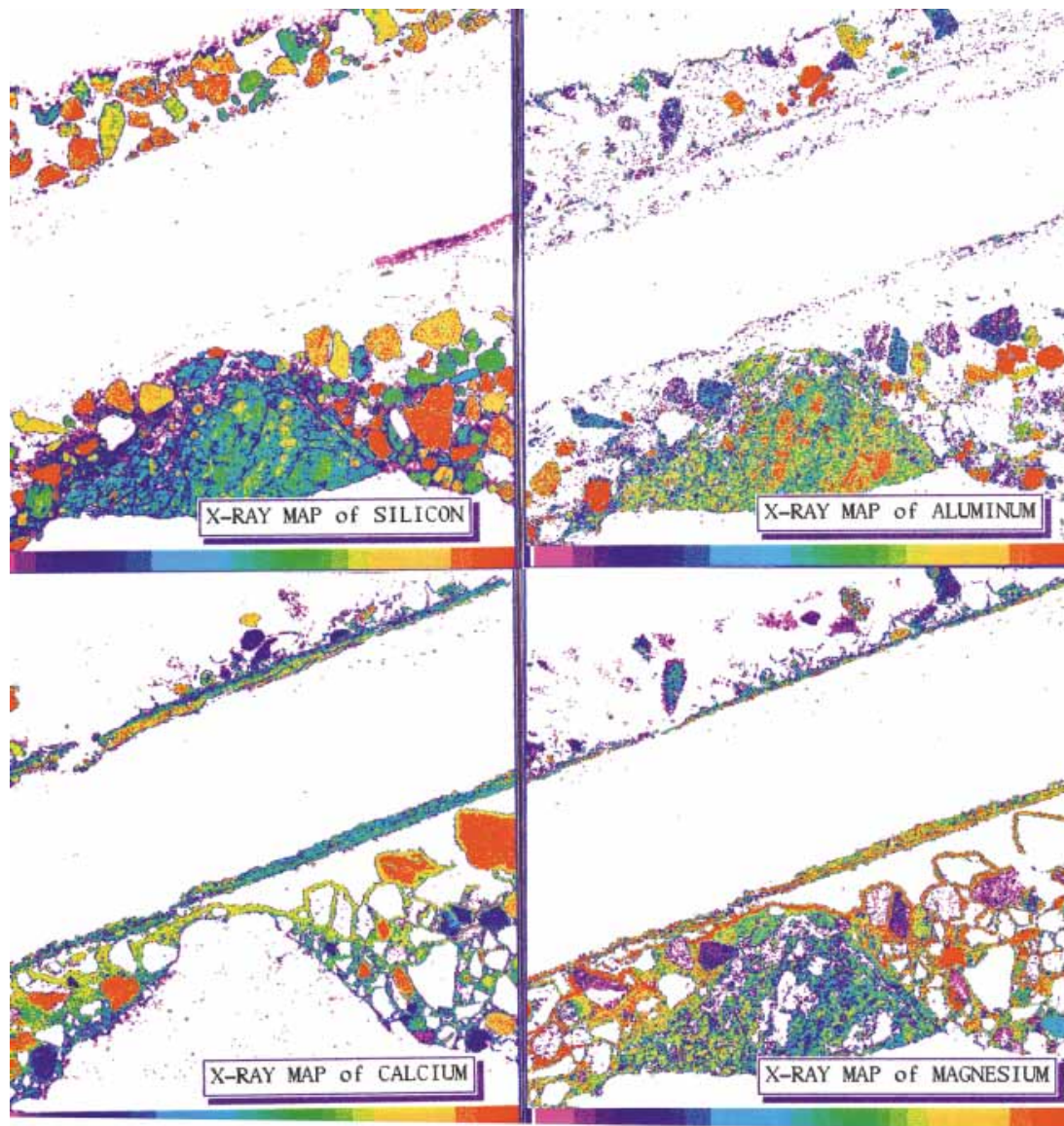
monly completely encased in the acanthite indicates that they must have grown in the early stages of diagenesis, before silver dissolution and reprecipitation of the argentiferous minerals.

DEDICATION AND ACKNOWLEDGEMENTS

This paper is dedicated to Louis J. Cabri in recognition of his many, varied, and significant contributions that have enhanced our understanding of ore minerals. His work, from phase-equilibrium studies to trace-element analysis, has advanced our knowledge of precious metals and the manner in which they are distributed in the Earth's crust. More importantly, he has been a friend and mentor to countless numbers of young aspiring mineralogists.

We are grateful John L. Jambor, Peter A. Williams, and Robert F. Martin for their editorial work that has much improved this manuscript, and to Mark Fortney, who assisted with illustrations.
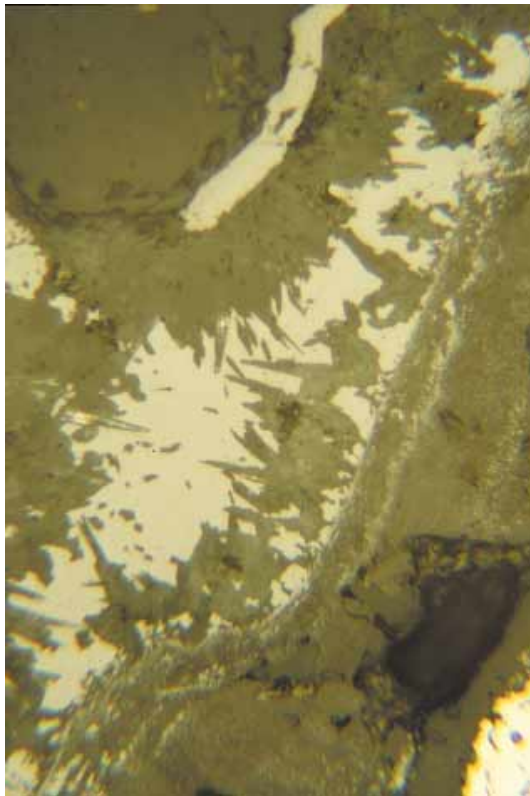
FIG. 9.   Needle-like crystals of calcium carbonate (likely aragonite) occur around the margins of many of the enclosing sedimentary particles and extend into what were initially open voids between the grains. Subsequent precipitation of the acanthite has infilled the interstices and engulfed the needles.

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