

## Possibility of Bacteria-Induced Corrosion of Ancient Bronze Mirrors Found in Ground\*

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Excavated bronze objects, depending on how long they have been in the ground and under what conditions, are generally corroded externally as well as having intricately corroded layers inside. To date, our group has performed metallurgical investigations on 18 ancient bronze mirrors and confirmed that pure copper lumps and several varieties of unidentified corrosion products have formed on the surface of the mirrors and in the corroded layers. Accordingly, we performed investigations to identify the corrosion products using an electron probe micro analyzer (EPMA), a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS), a micro-X-ray diffraction analyzer ( $\mu$ -XRD), and an X-ray photoelectron spectroscope (XPS), and discussed the possibility that bacteria play a role in inducing corrosion in ancient bronze mirrors. The results are as follows; (1) Amorphous  $\text{SiO}_2$  had formed in the outermost corroded layer I. (2)  $\text{Cu}_2\text{O}$  (cuprite) and  $\text{Cu}(\text{OH})_2$  had formed in the layers II and III, which comprise the first two internal layers adjacent to layer I. (3)  $\text{Cu-Sn-Pb}$ -complex oxide had formed in layer IV, the next internal layer. Small amounts of  $\text{PbSO}_4$  and an Sn-organic compound were also detected. (4) We observed that  $\text{Cu}_2\text{S}$  (chalcocite) forms like mold on the polished surface of the corroded layers, especially notable on layer IV, after being mechanically polished and left to stand for about one month.  $\text{Cu}_2\text{S}$  is presumed to be the resultant of sulfate reducing bacteria. (5) Numerous pure copper lumps appeared in layers or particles and tended to form in the vicinity of layer IV. (6) The evidence from these analyses suggest that microorganisms could have been the cause of the corrosion found in ancient bronze mirrors excavated from the ground.

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**Keywords:** ancient bronze mirror, corrosion in clay, resultant by corrosion, instrumental analysis, pure copper lump, amorphous silicon(IV) dioxide, copper(I) oxide, copper(II) hydroxide, lead(II) sulfate, copper(II) sulfide, microbial corrosion

### 1. Introduction

Excavated bronze objects, depending on how long they have been in the ground and under what conditions, are generally corroded externally as well as having intricately corroded layers inside. To date, our group has performed metallurgical investigations on 18 ancient bronze mirrors and confirmed that pure Cu lumps and several varieties of unidentified corrosion products have formed on the surface of the mirrors and in the corroded layers.<sup>1)</sup> Accordingly, we performed investigations to identify the corrosion products using an electron probe micro analyzer (EPMA), a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS), a micro-X-ray diffraction analyzer ( $\mu$ -XRD), and an X-ray photoelectron spectroscope (XPS). Here we discuss the possibility that bacteria play a role in inducing corrosion in ancient bronze mirrors.

### 2. Samples and Experimental Conditions

The bronze mirror focused on in the present investigation is the sample KU-E produced during the Eastern Han Dynasty period. It was in this mirror that the most typical types of corrosion products had been observed in our previous study.<sup>1)</sup> The external appearance of the mirror is shown in Fig. 1. A small piece was obtained as a sample from the frame of the mirror as indicated by arrows in the photograph. A part of the sample piece was embedded in

epoxy resin, polished to a mirror surface and analyzed by EMPA, EDS and  $\mu$ -XRD. From the rest of the sample piece, another sample was cut out with a diamond blade, ultrasonically cleaned in ethanol, and analyzed by XPS.

The equipment and the measurement conditions for the analyses by EMPA, EDS,  $\mu$ -XRD and XPS were as follows. EPMA; JXA-8900 (JEOL), accelerating voltage: 15 kV, radiation current: 0.05  $\mu\text{A}$ , correction method: metal ZAF (metal segments), oxide ZAF (oxide). EDS; JED-2200, JSM-5900 LV (JEOL), accelerating voltage: 20 kV, radiation current: 1.0 nA, correction method:  $\Phi(\rho_z)$ , radiation time: 100 s.  $\mu$ -XRD; Rint2500 (Rigaku Denki), X-ray:  $\text{CrK}\alpha$ , Voltage: 40 kV, current: 100 mA, radiation angle:  $30^\circ$ , X-ray beam diameter: approx. 100  $\mu\text{m}$ . XPS; JPS-9010MC (JEOL), X-ray:  $\text{Mg K}\alpha$ , Pass energy: 50 eV or 30 eV, power: 300 W, beam diameter: approx. 200  $\mu\text{m}\Phi$ .

### 3. Results and Discussion

#### 3.1 Overview and optical microscopic observation of the cross section of the sample KU-E

Both the back face (a) and the front face (b) of the mirror shown in Fig. 1 were classified into three categories depending on the color: matte but bright aeruginous parts, brown parts, and brownish gray parts. The patterns on the back face of the mirror still largely retained their original form, although their sharpness was a little degraded by the rust on the surface.

Figure 2 shows the optical micrographs of the cross section of the sample KU-E. As mentioned in the previous report,<sup>1)</sup> corrosion had developed from the surface to deep inside the

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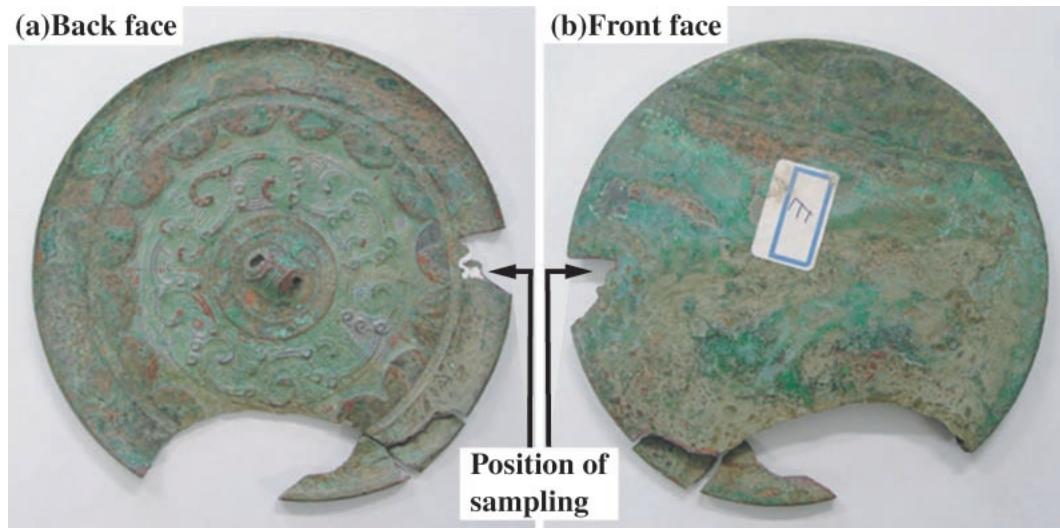


Fig. 1 Appearances of the ancient bronze mirror (KU-E) investigated here.

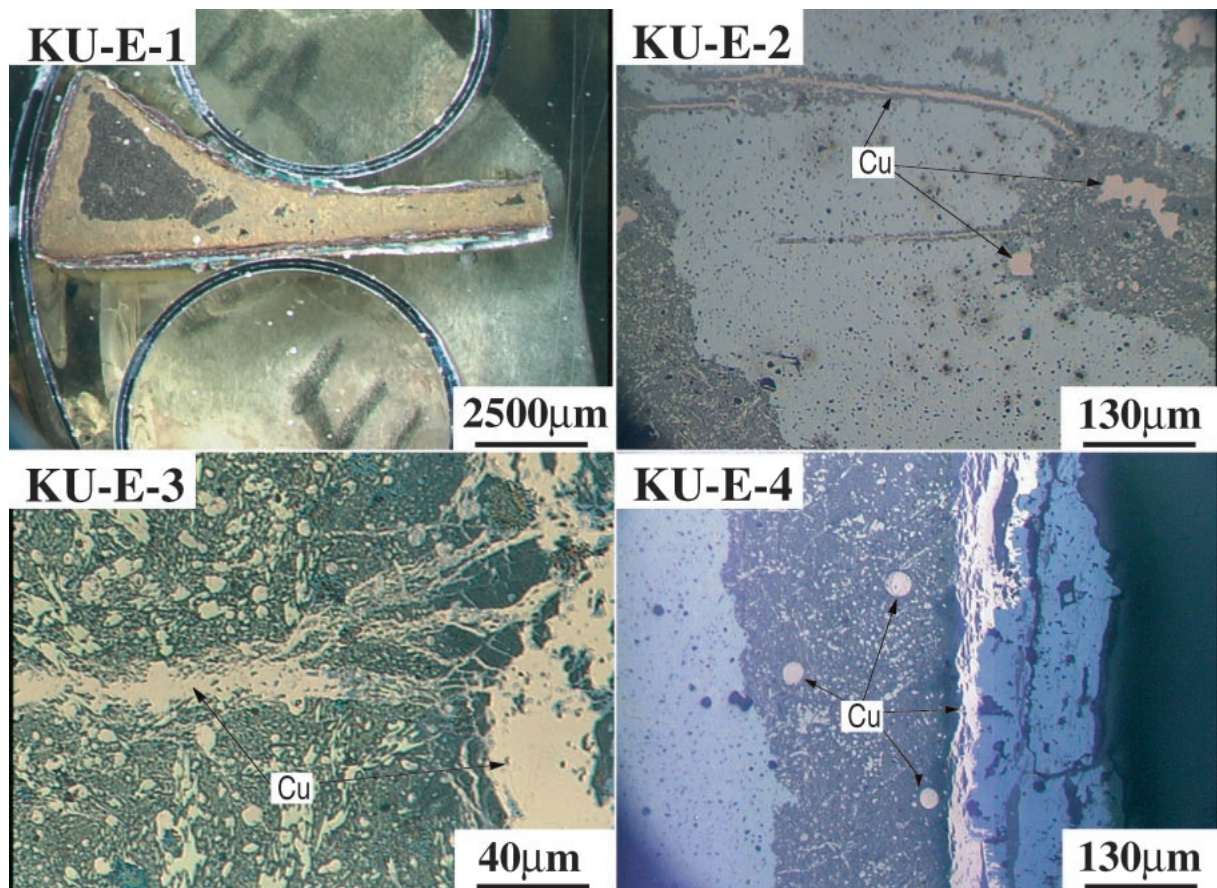


Fig. 2 Optical micrographs of vertical sectional views of the ancient bronze mirror (KU-E).

mirror. As is clear from KU-E-1, only the core of the mirror frame, which is the thickest part, was unaffected by corrosion, whereas the thinner centerpiece of the mirror was corroded throughout. As can be seen in figures KU-E-2 and KU-E-3, pure-copper colored structure was observed in the forms of a layer, granules and zigzag lines, which are presumed to be one kind of corrosion products. Figure KU-E-4, which is the cross section near the surface of the front face, shows that the corrosion products had formed layers from the

surface (the right side of the figure) to the inside. The bright blue gray part in the left side of the figure was a non-corroded matrix.

### 3.2 Elemental distribution mapping of the cross section of the sample KU-E

Figure 3 shows distributions of the main elements detected on the cross section of the sample. Figure 3(a) is the composition image obtained by SEM. Figures (b)–(f) show



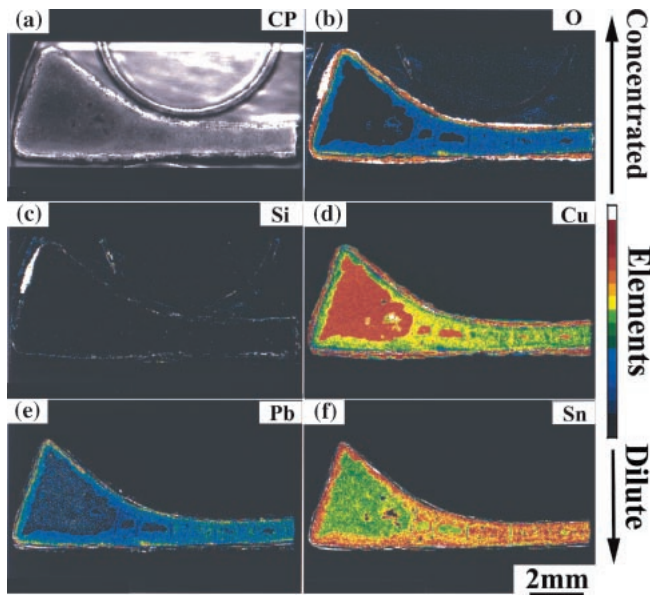


Fig. 3 Color Mapping figures in the ancient bronze mirror (KU-E).

concentrations of the elements indicated by colors. Shown as a color scale on the right side of the figure, the colors white, red, yellow, green, blue and black denote concentrations from high to low. An inspection of these figures clearly shows dramatic changes in the colors, thus we conclude that the alloy was inhomogeneous.

The figures (b) and (c) make it clear that a thin layer where O and Si coexist had formed on the surface of the mirror. Especially on an outer part of the frame, there was a dense, thick layer of O and Si. In the figure (d), Cu concentration was high on the surface and in the core of the frame, but relatively low in the corroded layers. The Pb distribution (e) shows a distinct difference between the concentrations in the corroded layers and the non-corroded matrix. The Sn distribution (f) was opposite to the Cu distribution (d); concentration was higher in the corroded layers than in the non-corroded matrix.

### 3.3 Chemical composition analyses by EPMA and EDS

As is shown in Fig. 2, KU-E-4, several layers of corrosion can be observed between the mirror surface and the inside. In order to establish the chemical composition of the corroded layers, analyses using EPMA and EDS were performed. At first, we used EPMA to measure not only main elements but also impurities. However in the course of investigation, it was

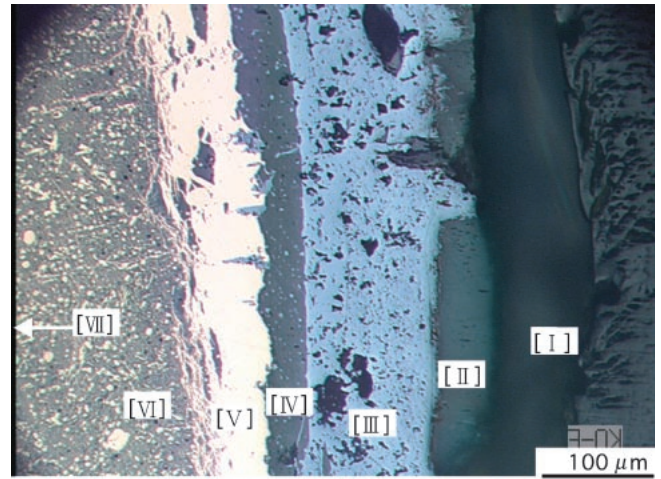


Fig. 4 Optical micrograph of vertical sectional view of the ancient bronze mirror (KU-E); layers [I] to [VII] are subject to chemical composition analyses by EDS and identification of phases by  $\mu$ -XRD and XPS analyses.

decided that the purposes of the study could be accomplished by measuring main elements using EDS analysis.

Figure 4 shows the layers subjected to chemical composition analysis.

Layer I, the outermost layer: a black translucent layer approximately 100  $\mu$ m thick.

Layer II, the second layer from the surface: a dark green layer approximately 50  $\mu$ m thick, formed discontinuously. Layer III, the third layer from the surface: a light ash gray layer approximately 130  $\mu$ m thick, runs parallel to the mirror surface. Layer IV, the fourth layer from the surface: the dark blue layer approximately 30  $\mu$ m. A distinct boundary between layers III and IV was observed. Layer V, the fifth layer from the surface, shows the pure copper color. The boundary between layer IV and V was revealed to be an irregular line. Layer VI, the sixth layer from the surface: a layer composed of particles and linear lumps of pure Cu, shown on the leftmost of the figure. There was a seventh area of non-corroded matrix, not shown in the figure.

The results of the EPMA and EDS analyses of layers I to VII are summarized in Table 1. The chemical compounds expected from the observed elemental composition values are also shown.

As a result of the analyses of the outmost layer I, Cu of 2.1 mass% and Pb of 4.1% were detected. However, main elements were Si and O, and the compound is considered to

Table 1 Analyzed chemical compositions and predicted chemical compounds on the micro areas of sectional surfaces of the sample KU-E.

Layers	Analyzed chemical compositions (mass%)					Predicted chemical compounds and stoichiometric values (mass%)					
	Cu	Sn	Pb	Si	O	Chemical compositions	Cu	Sn	Pb	Si	O
I	2.1	0.2	4.1	47.5	46.1	SiO <sub>2</sub>	0	0	0	40.84	59.16
II	65.9	0.2	1.3	0.4	32.2	CuO <sub>2</sub> (Cu(OH) <sub>2</sub> )	66.51	0	0	0	33.49
III	89.3	0.2	0.2	0.1	10.2	Cu <sub>2</sub> O	88.82	0	0	0	11.18
IV	12.5	43.5	19.8	0.3	23.9	Cu–Sn–Pb oxide	—	—	—	0	—
V	98.2	0.2	0.4	0.1	1.1	Cu	100	0	0	0	0
VII	71.4	24.2	2.8	0.1	1.5	(Cu–Sn–Pb)	—	—	—	0	0

Chemical compositions of layer VI are not described in the table because it was a mixture of corroded and non-corroded areas.

be silicon dioxide, the O value of which is smaller than the stoichiometric value. In layer II, amounts of Sn, Pb and Si were small and the main elements were Cu and O. Estimating from the stoichiometric value, this corresponds to  $\text{Cu(IV)O}_2$ . However, the ionic valency of Cu in  $\text{CuO}_2$  is four, therefore this is unlikely to be the oxide.<sup>2)</sup> As we did not take H into account in the analyses, it is likelier that the compound is  $\text{Cu(OH)}_2$ . In layer III, the main elements were Cu and O. Based on the stoichiometric ratio, we judge this to be  $\text{Cu}_2\text{O}$ . In layer IV, Cu, Sn, Pb and O were clearly detected, in addition to a very small amount of Si. This layer is considered to be a compound oxide of Cu, Sn and Pb. In layer V, although very small amounts of Sn, Pb, Si and O were detected, it is decidedly a pure Cu layer of 98% purity. Although pure Cu lumps in corroded layers of bronze mirrors have been reported,<sup>1,3)</sup> mechanism of the production is not identified yet. Layer VI is considered to be a mixture of granular pure Cu, non-corroded matrix and a mixed oxide of Cu, Sn and Pb. Layer VII is a non-corroded matrix. The composition of the original alloy of the mirror is considered to be high Sn bronze with Pb, containing about 3 mass% of Pb and about 24 mass% of Sn.

### 3.4 Phase identification by $\mu$ -XRD

In order to identify more specifically the various corrosion products expected from the composition values obtained in the previous section, we identified the phases using  $\mu$ -XRD. We analyzed the rectangular areas circumscribed by four straight lines as shown in Fig. 5. The areas were exposed to an X-ray beam 100  $\mu\text{m}$  in diameter. Figures 6(a) and (b) show the X-ray diffraction patterns obtained.

In layer I, diffraction peaks were not detected, leading us to assume that it is in an amorphous state. In layer II, peaks were detected which correspond to  $\text{Cu(OH)}_2$  (JCPDS: 35-505) and  $\text{Cu}_2\text{O}$  (JCPDS: 5-0667), with both peaks overlapping. The interplanar spacings of the layers of crystalline substances whose presence is indicated by the numbered peaks in the figures are shown in Table 2 for reference.

For layer III, results that strongly indicate  $\text{Cu}_2\text{O}$  were

Table 2 Interplanar spacings for the corroded layer II in the sample KU-E; peak numbers correspond to those in Fig. 6(a)(II).

Peak number	<i>d</i> (nm)	Peak number	<i>d</i> (nm)	Peak number	<i>d</i> (nm)
1	0.3714	13	0.2125	25	0.1496
2	0.3042	14	0.2059	26	0.1476
3	0.2992	15	0.1988	27	0.1473
4	0.2851	16	0.1944	28	0.1458
5	0.2782	17	0.1895	29	0.1420
6	0.2620	18	0.1860	30	0.1393
7	0.2522	19	0.1831	31	0.1385
8	0.2463	20	0.1812	32	0.1310
9	0.2351	21	0.1789	33	0.1271
10	0.2315	22	0.1676	34	0.1220
11	0.2274	23	0.1613	35	0.1205
12	0.2185	24	0.1513	36	0.1192

obtained. In layer IV, diffraction peaks correspond to pure Cu and unidentified small peaks were also detected. It is clear from Fig. 5-IV that the segment contains not only layer IV but also layer V. Therefore, the diffraction peaks obtained from layer V were eliminated from the diffraction pattern of segment IV of Fig. 6(b), and it was concluded that layer IV is amorphous-like or in an amorphous state. We came to this conclusion based on the results of our previous investigation<sup>4)</sup> of a bronze mirror produced in the Eastern Han Dynasty where the layer equivalent to layer IV in the present investigation is definitely in an amorphous state.

Layer V is considered to be pure Cu from the diffraction pattern shown in Fig. 6(b)-V.

From the diffraction pattern of layer VII, which is non-corroded matrix,  $\text{Cu}_{327.92}\text{Sn}_{88.08}$  (JCPDS: 30-0511) was detected as a main component and small amounts of  $\alpha$  Cu (JCPDS: 4-0836) and  $\text{Cu}_{5.6}\text{Sn}$  (JCPDS: 31-0487) were also detected.

### 3.5 Identification and atomic-state analysis of the corrosion products by XPS

Corrosion products in the corroded layers III, V and VII in

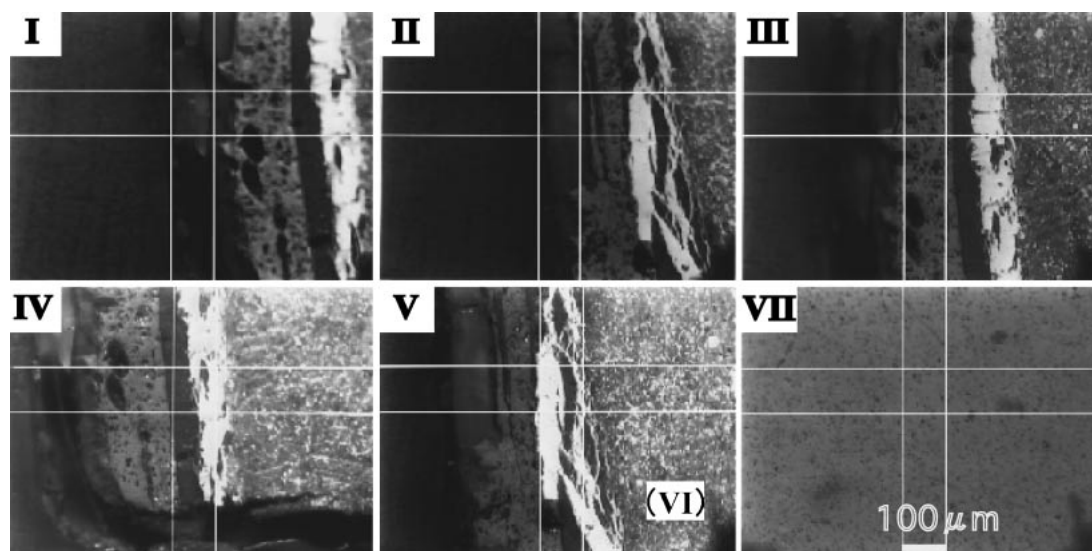


Fig. 5  $\mu$ -XRD analyzed positions on the ancient bronze mirror (KU-E).





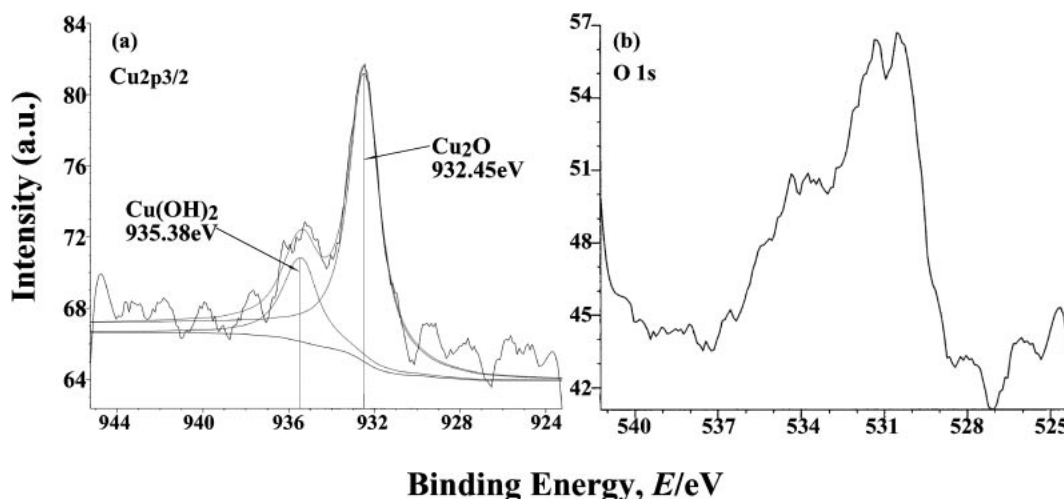


Fig. 9 Cu<sub>2p</sub>3/2 and O1s photoelectron spectra of layer (II) in Fig. 4 of the ancient bronze mirror (KU-E).

pattern, a quantitative analysis was also made. As a result, two kinds of compounds, Cu<sub>2</sub>O and Cu(OH)<sub>2</sub>, 77.6% and 22.4% by mass% respectively, were detected. The total oxygen content in layer II was 16.0%. However, according to the composition analysis of layer II by EDS, O content was 32.2%. There is a large difference between the two results in terms of oxygen content. One possible explanation is that, in the XPS analysis, both the Cu<sub>2</sub>O layer and Cu(OH)<sub>2</sub> layer were exposed to the X-ray beam. In either case, it is clear that Cu(OH)<sub>2</sub> exists in layer II.

Figure 10 shows the wide-scan spectral pattern of the corroded layer IV. Elements C, Cu, Sn, O and Pb were detected. The core-level spectral patterns of all the elements except for C are shown in Fig. 11. With regard to Cu (Cu<sub>2p</sub>3/2) in Fig. 11(a), metallic Cu oxide (11.2 mass%) and Cu<sub>2</sub>O (88.8 mass%) were detected. Figure 11(b) shows the spectral pattern of Sn<sub>3d</sub>5/2. Sn was detected in a very small amount as an organic compound (5.1 mass%) and as a mixed oxide of Sn and Pb. Figure 11(c) shows the spectral pattern of Pb<sub>4f</sub>7/2. Pb existed as PbSO<sub>4</sub> (19.0 mass%) and as a mixed oxides of

Pb, Sn and Cu (81.0 mass%).

From the results of XPS analysis in layer IV, it is noteworthy that an Sn-organic compound and S in the form of PbSO<sub>4</sub> were detected.

The above-mentioned results from EPMA, EDS,  $\mu$ -XRD and XPS are summarized in Table 3: Layer I was amorphous SiO<sub>1.7</sub>. Layer II contained Cu(OH)<sub>2</sub>, perhaps with some Cu<sub>2</sub>O. Layer III was a single layer of Cu<sub>2</sub>O. In layer IV, a mixed oxide of Cu, Sn and Pb and small amounts of an Sn-organic compound and PbSO<sub>4</sub> were detected. Layer V was a Cu layer of relatively high purity. Layer VI was a mixture of granular pure Cu, non-corroded matrix and a mixed oxide of Cu, Sn and Pb. Layer VII was a non-corroded area having a mass% ratio of Cu : Sn : Pb = 72.4 : 25.1 : 2.6, namely high Sn bronze.

When bronze objects corrode slowly in the ground over many years, complex compounds form as mentioned above. In order to clarify the mechanism by which these compounds are produced, it is necessary to identify the environment in the ground at the time the bronze objects were buried. Unfortunately, the precise environmental conditions cannot be ascertained. However, one thing can be stated with certainty: not only the bronze mirror KU-E but a lot of bronze objects are being corroded in a similar way to a greater or lesser degree. Based on this observation, it can be assumed that the mirror KU-E was not in an unusual environment.

Further investigations are needed to identify the cause of the corrosion that developed while the objects were in the ground. However, we would like to focus attention on the following corrosion products detected in the present investigation: an Sn-organic compound and PbSO<sub>4</sub> detected in the corroded layer IV and amorphous silicon dioxide formed in layer I.

These results suggest the possibility of bacteria-induced corrosion in ancient bronze mirrors that have lain in the ground. In addition, from the information and survey results in other fields that support this contention,<sup>7-10)</sup> we made following inferences.

Firstly, reports exist on bacteria-induced corrosion of copper and copper alloy.<sup>11,12)</sup> This mechanism is yet to be clarified but growth of sulfate-reducing bacteria is said to

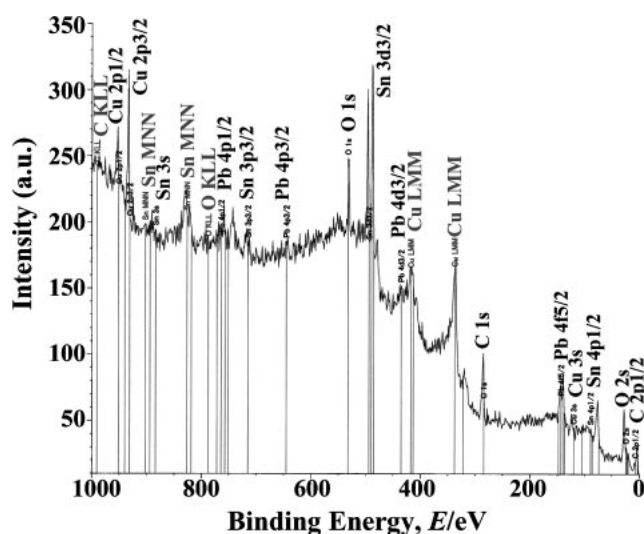


Fig. 10 Wide-scan spectral pattern of layer (IV) of the ancient bronze mirror (KU-E).

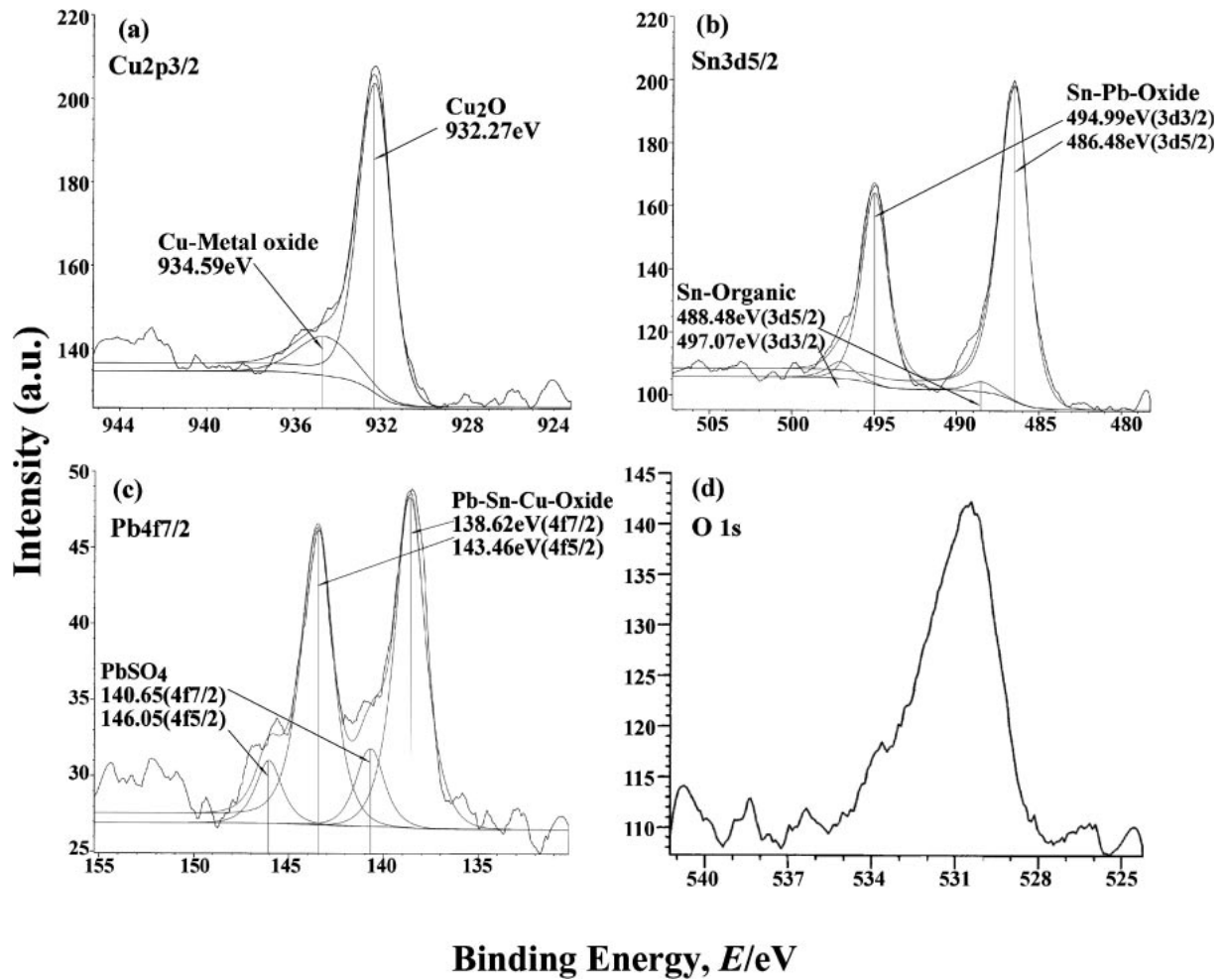


Fig. 11 Cu2p3/2(a), Sn3d5/2(b), Pb4f7/2(c) and O1s(d) photoelectron spectra of layer (IV) in Fig. 4 of the ancient bronze mirror (KU-E).

Table 3 Various kinds of corrosion products in the ancient bronze mirror (KU-E), decided by means of various instrumental analyzer.

Analytical methods	EDS (EPMA)	$\mu$ -XRD	XPS
Layers			
I	SiO <sub>2</sub>	Amorphous like	Amorphous SiO <sub>2</sub>
II	CuO <sub>2</sub> ? (Cu(OH) <sub>2</sub> ?)	Cu(OH) <sub>2</sub> +Cu <sub>2</sub> O	Cu(OH) <sub>2</sub> +Cu <sub>2</sub> O
III	Cu <sub>2</sub> O	Cu <sub>2</sub> O	*
IV	(Cu, Sn, Pb)-oxide	Amorphous	Mixtures of Cu-metal oxide, Cu <sub>2</sub> O, Sn-Pb-oxides, Pb-Sn-Cu oxide, Sn-organic, PbSO <sub>4</sub>
V	Pure Cu	Pure Cu	*
VI	Mixture of non-corroded and corroded portions	*	*
VII	Non-corroded ground alloy; Cu: 72.4%, Sn: 25.1%, Pb: 2.6%	Cu <sub>327.92</sub> Sn <sub>88.08</sub> + $\alpha$ -Cu+Cu <sub>5.6</sub> Sn	*

\*: Not analyzed.

produce corrosive sulfide. Specifically, sulfate-reducing bacteria deoxidizes SO<sub>4</sub><sup>2-</sup> and a large quantity of corrosive H<sub>2</sub>S, for instance, is produced and this corrodes Cu and Cu alloys.<sup>13)</sup>

In the present investigation, S was detected as PbSO<sub>4</sub>.

Coincidentally, it was also found through SEM examination in our laboratory that a mucedinous product formed on the polished surface of the corroded layers in the mirror KU-E, as shown in Fig. 12. We had polished and kept the sample in a desiccator for about one month at a temperature of 300 K and

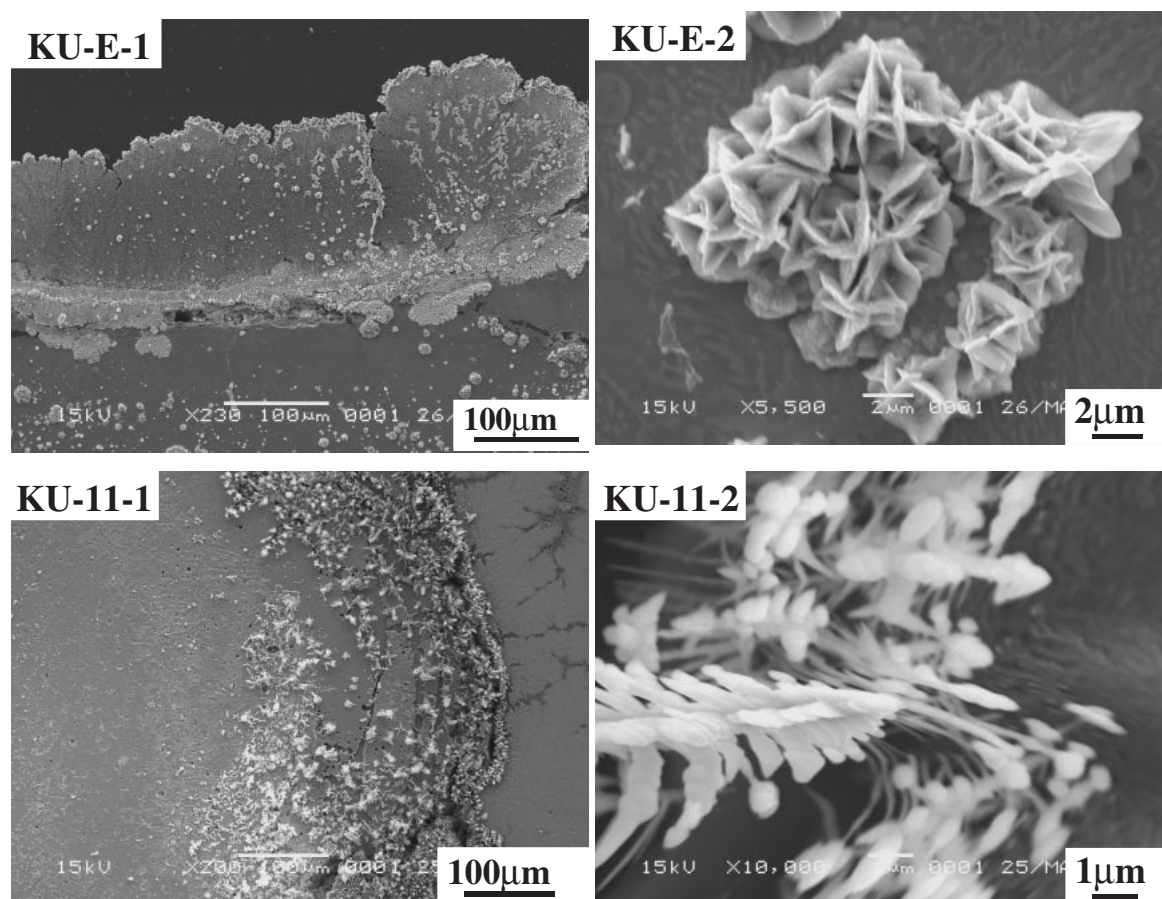


Fig. 12 Mucedinous products formed on the polished surfaces of the ancient bronze mirrors (KU-E) and (KU-11).

a humidity of 40%. As we observed a similar phenomenon in another sample KU-11 (produced during the Eastern Han Dynasty), we show the photographs in Fig. 12 for reference.

EDS analysis revealed that the mucedinous product was  $\text{Cu}_2\text{S}$ . It was not possible for the mirror to have been contaminated by S components, such as sulfuric acid, while in the pretreatment stage before the various analyses. It seems likely that sulfate-reducing bacteria have taken in S components from the surroundings and concentrated those S components while the bronze mirror was buried in the ground. However, sulfate-reducing bacteria are anaerobic. Thus we would not expect sulfate-reducing bacteria to deoxidize  $\text{SO}_4^{2-}$  to produce the  $\text{S}^{2-}$  of the  $\text{Cu}_2\text{S}$  on the polished surface exposed to the atmosphere. To resolve this apparent contradiction, we suggest that when the sample was polished by a wet process, sulfate-reducing bacteria residing in the corroded layers were hydrated and awakened from dormancy, activated their metabolism, and excreted  $\text{Cu}_2\text{S}$  to the surface.

Future tasks are to confirm whether or not corrosion-inducing bacteria exist in ancient bronze mirrors by using analytical instruments such as an electron microscope, and to identify the types of the bacteria by culturing them from samples taken from the corroded layers with assistance from microbiologists.

In the corroded layers, we confirmed that  $\text{PbSO}_4$ , an Sn-organic compound and other compounds such as amorphous silicon dioxide,  $\text{Cu}(\text{OH})_2$ , pure Cu,  $\text{Cu}_2\text{O}$ , etc. were being

produced. Although few investigations of the mechanism of such production have been carried out,<sup>14,15)</sup> all these investigations were made from an inorganic-chemical point of view. They did not go far enough in their analyses to clarify the cause of the corroded layers. There are no other reports on bacteria-induced corrosion of ancient bronze mirrors apart from the one presented here.

It is still premature to assert that bacteria have caused the corrosion found in ancient bronze mirrors. However, it is clear that bacteria are closely related to the alteration of metals in such processes as bio-leaching<sup>7)</sup> (seen in copper mines), bio-sorption<sup>8)</sup> (sorption of heavy-metal ion by bacteria), bio-remediation<sup>9)</sup> (restoration of environmental pollution by bacteria), and bio-mineralization<sup>10)</sup> (bacteria-induced concentration and mineralization of metal ions). In our living environment, we can also commonly find bacteria films referred to as “microbial mats”.<sup>16)</sup> The presence of granular metallic pure Cu and  $\text{SiO}_2$  has been confirmed in microbial mats produced in mine water taken from copper mines.<sup>17)</sup>

In microbial mats, production of metal compounds (mainly oxides), and  $\text{SiO}_2$  (mainly amorphous) are widely observed.<sup>17)</sup> As just mentioned, the mechanism of how metals and metallic compounds are altered by bacteria is yet to be clarified, but it would seem plausible that the amorphous silicon dioxide confirmed in the present investigation is a by-product of bacterial metabolism.

The evidence from these analyses suggests that bacteria



could have been the cause of the corrosion found in ancient bronze mirrors excavated from the ground. Corrosion can be a cause of deterioration of not only bronze cultural assets, but also various kinds of metal cultural assets. If the linkage with bacteria-induced corrosion is clarified, we may have to reconsider the storage techniques employed for metallic cultural assets.<sup>18)</sup>

#### 4. Conclusion

We have analyzed the corrosion products formed in an ancient bronze mirror corroded in the ground by various instrumental analyses and discussed how these corrosion products might have been generated. The results are as follows.

- (1) In the outermost corroded layer I, amorphous silicon dioxide had formed.
- (2) In layers II and III,  $\text{Cu}_2\text{O}$  and  $\text{Cu}(\text{OH})_2$  had formed.
- (3) In layer IV, a mixed oxide of Cu, Sn and Pb had formed. Small amounts of an Sn-organic compound and  $\text{PbSO}_4$  were also detected here.
- (4) Layer V was a thick layer of pure Cu.
- (5) Layer VI was a mixture of granular pure Cu, non-corroded matrix and a mixed oxide of Cu, Sn and Pb.
- (6) Mucedinous  $\text{Cu}_2\text{S}$ , presumed to be the waste product of sulfate-reducing bacteria, had formed on the surface of the corroded layers, which were left to stand for about one month after being mechanically polished. The formation of this substance was especially notable on layer IV.
- (7) The evidence from these analyses suggests that bacteria could have been the cause of the corrosion found in ancient bronze mirrors excavated from the ground.

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