Blackening of the Surfaces of Mesopotamian Clay Tablets Due to Manganese Precipitation

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Abstract

Blackening was observed on the surfaces of Mesopotamian clay tablets from Umma, Dilbat, Larsa, Ur, Babylon, Uruk, Sippar, and Nippur produced between the Third Dynasty of Ur and the Early Achaemenid Dynasty. Portable X-ray fluorescence analysis revealed that manganese was concentrated on the blackened surfaces. Rod-shaped materials with a length of 100 - 200 nm and a width of 30 nm were observed using a field emission scanning electron microscope. Distinct peaks were not necessarily obtained by micro-X-ray diffractometer analysis, but several samples of the black material showed peaks identifiable as buserite. These results may suggest that blackening on the surfaces of the clay tablets can be ascribed to the activity of manganese-oxidizing microbe. However, the size of the rod-shaped materials is too small compared to common bacteria.

Keywords

Clay Tablet, Mesopotamia, Maganese Concentration, Manganese-Oxidizing Microbe, Buserite

1. Introduction

Clay tablets were used as writing media in Mesopotamia, and cuneiform script was written on their surfaces. Clay tablets began to be used around 3300 BC; those made in the Third Dynasty of Ur, 2113-2006 BC, have been excavated most abundantly. The clay tablets record events related to agriculture, the economy, politics, and other matters.

In 2009, 2011, and 2012, the authors conducted non-destructive chemical analysis and magnetic susceptibility measurements on Mesopotamian clay tablets stored in the Yale Babylonian Collection of Yale University to
elucidate differences in the chemical composition between areas and the provenance of soil. Some of the results obtained in the investigation were published in Uchida et al. (2011) and Sterba et al. (2011). In the course of the study, the authors found blackening phenomena on the surfaces of the clay tablets. The blackened parts appear as spots or occupy wide areas. The blackening phenomena have previously been considered to be caused by soot attached on the surface during firing. However, chemical analysis using a portable X-ray fluorescence analyzer (pXRF) revealed that manganese is concentrated in the blackened parts. Blackening caused by manganese concentration on the surfaces of clay tablets has been reported previously (Laurito et al., 2005; Gütschow, 2012). However, the details of the formation mechanism have not yet been elucidated. Thus, in this study we focused on the blackening phenomena on the surfaces of the clay tablets and conducted a detailed study to determine the formation mechanism.

2. Methods

Non-destructive chemical analysis using an Innov-X Systems Delta Premium portable X-ray fluorescence analyzer (pXRF) with a Rh anode X-ray tube (4 W) was carried out on clay tablets showing blackening. The X-ray beam diameter is 9 mm. The test stand for the pXRF was used in the analysis. The measurement was conducted in “soil mode” using three different filters each for 20 sec (Beam 1 at 40 kV for U, Sr, Y, Zr, Th, Mo, Ag, Cd, Sn and Sb; Beam 2 at 40 kV for Fe, Co, Ni, Cu, Zn, W, Hg, As, Se, Pb, Bi and Rb; and Beam 3 at 15 kV for P, S, Cl, K, Ca, Ti, V, Cr, and Mn). The pXRF was calibrated in advance using 10 standard rock samples of the Geological Survey of Japan (JA-1, JA-2, JB-1b, JB-2, JB-3, JG-1a, JG-2, JGb-1, JR-1, and JR-2) (Imai et al., 1995). Calibration was conducted successfully for 17 elements: K (549), Ca (1389), Ti (65), V (16), Cr (14), Mn (73), Fe (264), Co (2), Ni (17), Cu (7), Zn (6), As (2), Rb (2), Sr (5), Y (1), Zr (2), and Pb (3). The figures in parentheses show standard deviations (ppm) of the chemical analysis in the average values of the clay tablets.

Samples for analyses were taken from blackened parts on the surfaces of clay tablets with no cuneiform script using a utility knife.

The chemical composition of the collected samples were determined using an electron probe X-ray microanalyzer (EPMA), which is composed of a JEOL JSM-6360 scanning electron microscope and an Oxford Instruments INCA ENERGY energy dispersive X-ray spectrometer. The accelerating voltage was 15 kV and the measuring time was fixed at 60 sec. The blackened parts of the clay tablets were analyzed using the EPMA; non-blackened parts were also analyzed as a control. The samples were coated with carbon. The chemical compositional information from the surface to a few μm in depth was obtained by the EPMA analysis in contrast to from the surface to a few mm in depth by the pXRF analysis.

Micro-X-ray diffraction analysis was conducted on the samples to identify the constituent minerals of the clay tablets and also the black materials. The analysis was conducted using a Rigaku RINT-RAPID micro-X-ray diffractometer (micro-XRD) with an X-ray tube with a Cu target. The tube current and voltage were 30 mA and 40 kV, and the measuring time was 30 min. A collimator with 100 μm φ was used in the measurement. The oscillating angles had a range of 7˚ - 14˚ for the ω axis (1˚/min) and −180˚ to +180˚ (6˚/min) for the φ axis.

Additionally, observations were conducted using a Hitachi S-4500S field emission scanning electron microscope (FE-SEM) on the samples taken from the black material of the clay tablets. The accelerating voltage was fixed at 15 kV. The samples were coated with platinum.

3. Blackening on the Surfaces of the Clay Tablets

The clay tablets investigated in this study are from Umma, Dilbat, Larsa, Ur, Babylon, Uruk, Sippar, and Nippur (Figure 1). The production periods of the studied tablets are from the Third Dynasty of Ur to the Early Achaemenid Dynasty (2113 BC to 330 BC). Economic or political events are described on the surfaces of the clay tablets.

The blackened parts caused by manganese precipitation occur as spots (NBC4846 and BCBT547), or as stains (NBC6240 and NBC30) (Figure 2). Occasionally a blackened part occupies a wide area on the surface of a clay tablet (NCBT2276 and YBC14659). Blackening is frequently observed on the surfaces of clay tablets, and more than 10% of clay tablets show blackening. The blackening phenomenon was seen on the tablets from all provenances investigated in this study. There is no correlation between the blackening phenomenon and the areas. It is considered that the black material was not formed in storage areas such as museums, but when the tablets were buried in soil.

The thickness of the black material on the surfaces of the clay tablets is less than 0.2 mm (Figure 3).
4. Results

4.1. Chemical Analysis Using pXRF

The results of the chemical analysis of the black material on the surfaces of the clay tablets using the pXRF are summarized in Table 1. Measurements were conducted on blackened surfaces and non-blackened surfaces of the clay tablets. As the surface is not completely covered by the black material even in the blackened part, and
Figure 3. Cross-sections of the black material on the surfaces of clay tablets from Larsa (Old Babylonian period).

| Area     | Period          | Sample no. | Ca   | K   | Ti  | Cr  | Mn  | Fe  | Co  | Ni  | As  | Pb  | Rb  | Sr  | Zr  | Cu  | V   | Y   |
|----------|-----------------|------------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Umma     | Ur III          | YBC14659   | Clay | 124703 | 372727 | 3121 | 269 | 3122 | 39424 | 27 | 353 | 467 | 20 | 55 | 54.2 | 388 | 124 | 102 | 147 | 22.8 |
|          | Black part      | 90264      | 38577 | 3247 | 401 | 7193 | 37662 | 25 | 446 | 389 | 16 | 22 | 48.3 | 392 | 113 | 148 | 150 | 22.6 |
| Dilbat   | Early Neo-      | MLC597     | Clay | 105871 | 22461 | 4126 | 319 | 1510 | 48395 | 25 | 359 | 241 | 12 | 25 | 65.6 | 422 | 137 | 95 | 141 | 21.2 |
|          | Neo-Babylonian  | NCBT547    | Clay | 111832 | 26923 | 4055 | 291 | 4397 | 50138 | 31 | 335 | 809 | 21 | 21 | 62.1 | 906 | 136 | 150 | 164 | 25.9 |
| Larsa    | Neo-Babylonian  | YBC5148    | Clay | 110804 | 21290 | 3306 | 190 | 934 | 38865 | 24 | 284 | 199 | 8.1 | 16 | 53   | 309 | 114 | 118 | 127 | 20.2 |
|          | Black part      | 130388     | 15467 | 3187 | 167 | 2615 | 38082 | 18 | 438 | 171 | 12 | 10 | 37.1 | 309 | 113 | 110 | 112 | 22.3 |
| Urum     | Ur III          | NBC5658    | Clay | 13470 | 23915 | 37232 | 174 | 4189 | 36059 | 23 | 462 | 85 | 11 | 24 | 54.6 | 331 | 111 | 48 | 113 | 20.2 |
| Babylon  | Neo-Babylonian  | NBC4868    | Clay | 123245 | 14910 | 4307 | 261 | 987 | 51182 | 28 | 404 | 450 | 14 | 20 | 47.3 | 380 | 152 | 135 | 135 | 26.1 |
|          | Black part      | 128912     | 15593 | 4425 | 226 | 4730 | 47792 | 23 | 3022 | 235 | 15 | 21 | 42.1 | 395 | 148 | 109 | 140 | 25.6 |
| Urak     | Neo-Babylonian  | NBC6219    | Clay | 100031 | 28441 | 3701 | 224 | 1619 | 45576 | 26 | 311 | 260 | 12 | 34 | 58.3 | 379 | 124 | 450 | 123 | 23.8 |
|          | Black part      | 87265      | 29976 | 3967 | 236 | 10203 | 43361 | 12 | 616 | 171 | 15 | 25 | 52.6 | 361 | 125 | 104 | 174 | 20.4 |
| Ummah    | Ur III          | NBC9332    | Clay | 126915 | 12135 | 3825 | 131 | 1283 | 46025 | 26 | 392 | 218 | 10 | 35.5 | 299 | 124 | 68 | 122 | 22.5 |
|          | Black part      | 129335     | 15354 | 3641 | 184 | 9171 | 44830 | 20 | 741 | 389 | - 35.5 | 346 | 130 | 90 | 160 | 24.6 |
| Umma     | Ur III          | NCBT2276   | Clay | 114890 | 18394 | 2306 | 156 | 797 | 26948 | 20.6 | 228 | 58 | 10.6 | 16 | 51.0 | 246 | 94 | 36 | 77 | 15.8 |
|          | Black part      | 86184      | 19079 | 2790 | 160 | 13588 | 32707 | 21 | 868 | 80 | 14 | 27 | 51.1 | 270 | 93 | 55 | 154 | 19.2 |
| Larsa    | Old-Babylonian  | YBC5148    | Clay | 98000 | 21457 | 3058 | 203 | 21996 | 35638 | 10 | 501 | 114 | 21 | 47 | 50 | 322 | 108 | 113 | 263 | 20.5 |
|          | Black part      | 31799      | 65720 | 4916 | 1863 | 993 | 55408 | 25 | 784 | 156 | 22 | 73 | 90 | 231 | 129 | 92 | 195 | 24 |
| Nippur   | Ur III          | YBC13363   | Clay | 52286 | 50108 | 4409 | 1317 | 20275 | 51628 | 18 | 844 | 142 | 23 | 40 | 81 | 265 | 127 | 68 | 259 | 23.5 |
|          | Black part      | 110706     | 27767 | 3878 | 233 | 4060 | 43090 | 19 | 370 | 456 | 18 | 43 | 50.7 | 374 | 122 | 266 | 121 | 22.4 |
| Sippar   | Early Achaemenid| NBC6240    | Clay | 86802 | 26993 | 4233 | 257 | 11806 | 43924 | 11 | 507 | 290 | 9 | 33 | 50 | 356 | 124 | 189 | 128 | 21.1 |
|          | Black part      | 125944     | 36130 | 3837 | 462 | 1685 | 43057 | 18 | 367 | 409 | 13 | 20 | 51.1 | 559 | 131 | 103 | 191 | 23.6 |

Table 1. Results of the chemical analysis of the black material and clay tablets using pXRF.
also the black material is thin (less than 0.2 mm in thickness) (Figure 3), it is certain that there is some contribution from the clay itself to the analytical results.

Figure 4 shows the ratio of the chemical composition of the blackened part to that of non-blackened part of the clay tablets. The results show that manganese is concentrated in the blackened parts 2 - 20 times more than in the non-blackened parts. Next to manganese, nickel is concentrated in the blackened parts (1 - 7 times). Although not present in every tablet, vanadium, chromium, zinc, arsenic, and lead are concentrated in the blackened parts.

4.2. Chemical Analysis Using EPMA

EPMA analysis was conducted on four clay tablets: NBC6219, NBC30, BCBT2276, and YBC5148. We analyzed black material on the surfaces of the clay tablets and also the clay itself for comparison. The analysis was carried out at three points on the black material and at three points on the clay for each sample. The results are summarized in Table 2, and the points analyzed are shown in Figure 5. In the calculation, Mn was treated as Mn⁴⁺ and Fe as Fe⁷⁺.

The EPMA analysis reflects the chemical composition in shallower parts of the tablets than the pXRF analysis does. Therefore, the EPMA analysis gives us more accurate information on the chemical composition of the black material. However, EPMA is not suitable for analysis of minor elements because of its low sensitivity.

The results show that manganese is concentrated in the black material 20 - 240 times more than in the original clay tablets. For Fe, the content is low in the black material compared with the original clay tablet. Therefore, it is considered that the black material is composed essentially of manganese. Although Si, Al, Mg, and K were also detected in the black material, these elements are considered to be derived from the minerals making up the clay tablets. A few percent of S was detected in the black material, but the S content in the clay tablets (non-black material) is usually less than 1%. This fact suggests that S is concentrated more or less in the black material. The Ca content is also high in the black material, and so it is considered that gypsum (CaSO₄·2H₂O) exists in the black material. In clay tablets NBC6219, NBC30, and YBC5148, a considerable amount of Ca compared with S is contained in the black material. This may suggest that Ca is present in calcite as well as in gypsum.

4.3. Micro-XRD Analysis

Table 3 summarizes the constituent minerals of the clay tablets, identified using micro-XRD. Quartz and calcite are identified from all clay tablets. Dolomite is found in several clay tablets, as is gypsum. However, it is consi-
Table 2. Results of the chemical analysis of the black material and clay tablets using the EPMA. The totals were normalized to 100%.

|       | NBC6219 |          | NBC30 |
|-------|---------|----------|-------|
|       | Black-1 | Black-2  | Clay-1 | Black-1 | Black-2  | Clay-1 | Clay-2 | Clay-3 | Black-1 | Black-2  | Clay-1 | Clay-2 | Clay-3 |
| Na    | 0.58    | 0.47     | 0.62   | 0.88    | 1.13     | 1.09    | 0.58   | 0.41   | 0.28    | 1.67     | 0.96   | 1.37   |
| Mg    | 2.89    | 2.82     | 3.05   | 4.89    | 4.93     | 4.50    | 2.85   | 2.94   | 2.35    | 3.63     | 3.39   | 2.89   |
| Al    | 4.43    | 4.49     | 4.84   | 8.72    | 8.17     | 7.82    | 3.09   | 3.44   | 4.98    | 6.93     | 7.02   | 11.15  |
| Si    | 13.70   | 13.74    | 14.33  | 25.10   | 24.61    | 23.41   | 8.69   | 6.80   | 6.51    | 21.33    | 23.99  | 21.96  |
| S     | 3.60    | 4.84     | 4.59   | 0.12    | 0.90     | 0.07    | 1.64   | 3.15   | 4.11    | 0.03     | 0.04   | 0.03   |
| Cl    | 0.12    | 0.33     | 0.23   | 0.16    | 0.17     | 0.12    | 2.08   | 3.05   | 4.29    | 0.62     | 0.23   | 0.14   |
| K     | 1.61    | 1.64     | 1.52   | 2.67    | 2.13     | 2.35    | 0.60   | 0.23   | 0.46    | 1.95     | 4.10   | 7.03   |
| Ca    | 12.67   | 9.51     | 10.29  | 3.76    | 5.81     | 4.44    | 22.22  | 25.59  | 27.40   | 15.22    | 9.89   | 5.24   |
| Mn    | 13.06   | 13.75    | 10.79  | 0.21    | 0.14     | 0.27    | 17.30  | 13.96  | 7.98    | 0.20     | 0.13   | 0.34   |
| Fe    | 5.09    | 5.15     | 6.52   | 7.87    | 6.21     | 6.62    | 3.30   | 3.09   | 4.41    | 5.84     | 6.43   | 6.13   |
| O     | 42.23   | 43.26    | 43.23  | 45.61   | 45.79    | 44.32   | 37.66  | 37.33  | 37.22   | 42.58    | 43.82  | 43.72  |
| Total | 100     | 100      | 100    | 100     | 100      | 100     | 100    | 100    | 100     | 100      | 100    | 100    |

Table 3. Constituent minerals of the clay tablets identified using a micro X-ray diffractometer.

| Area            | Period              | Sample no. | Quartz | Calcite | Pyroxene | Gypsum | Dolomite | Plagioclase | Buserite |
|-----------------|---------------------|------------|--------|---------|----------|--------|----------|-------------|----------|
| Umma Ur III     | YBC14659            | ++        | +      | +       | +        | +      |
| Dilbat Early Neo-Babylonian | MLC597   | ++        | +      | +       | +        | +      |
| Larsa Neo-Babylonian | NCBT547 | ++        | +      | ++      | +        | +      |
| Ur Ur III       | NBC5658             | ++        | ++     | +       | +        | +      |
| Babylon Neo-Babylonian | NBC4846 | ++        | +      | ++      | +        | +      |
| Babylon Neo-Babylonian | NBC6219 | ++        | +      | +       | +        | +      |
| Uruk Neo-Babylonian | YBC9932 | ++        | +      | ++      | +        | +      |
| Umma Ur III     | NCBT2276            | ++        | +      | ++      | +        | +      |
| Larsa Old-Babylonian | YBC5148 | ++        | +      | +       | +        | +      |
| Umma Ur III     | YBC13363            | ++        | +      | +       | +        | +      |
| Sippar Early Achaemenid | NBC6240 | ++        | +      | +       | +        | +      |
| Nippur Ur III   | NBC30               | ++        | +      | +       | +        | +      |

Note: ++: a large amount; +: a small amount.

It was also noted that gypsum was formed on the surface of the clay tablets when they were buried in soil. Additionally, small amounts of plagioclase and pyroxene were identified from some clay tablets.
In the micro-XRD analysis, a 10 Å manganese mineral was detected in the black material of clay tablets YBC5148, NBC30, and NCBT2276 (Figure 6). Although a large amount of manganese was present in the black material, XRD peaks attributable to manganese minerals were not necessarily obtained from all the clay tablets. This fact may suggest that manganese exists as amorphous materials. Buserite and todorokite are the candidates for 10 Å manganese minerals. To identify them, samples with black material were placed in an oven at 105˚C for 24 h, and were measured with the micro-XRD. As a result, birnessite newly appeared instead of the 10 Å manganese mineral. This suggests that the 10 Å manganese mineral in the black material is not todorokite, but buserite (Sato et al., 2000). Buserite is known to be a major constituent mineral of manganese nodules on the sea floor (Burns et al., 1983; Giovanoli et al., 1971; Usui & Someya, 1997). The participation of manganese-oxidizing bacteria in the formation of manganese nodules was pointed out by LaRock and Ehrlich (1975), Thiel (1925), and Wang and Müller (2009). Gypsum (CaSO₄·2H₂O) was changed into bassanite (CaSO₄·½H₂O) by dehydration when the samples were dried at 105˚C.

4.4. FE-SEM Observations

Rod-shaped materials with a length of 100 - 200 nm and a width of 30 nm were observed on the blackened surfaces of the clay tablets by the FE-SEM. Platy manganese-bearing crystals were also seen. It appears that rod-shaped materials were gathered and changed into platy crystals (Figure 7). This may suggest that platy manganese-bearing minerals were formed by recrystallization of the remains of the manganese-oxidizing mi-
Figure 6. X-ray diffraction patterns of the black material taken from clay tablets NBC30 and YBC5148, obtained using the micro-X-ray diffractometer. Abbreviations: Q, quartz; Pl, plagioclase; Cal, calcite; Gy, gypsum; Ba, bassanite; Bir, birnessite; and Bus, buserite.

Figure 7. FE-SEM images of the black material on the surfaces of the clay tablets.

crobe. However, the size of the rod-shaped materials is too small compared with common bacteria.

5. Conclusion

The pXRF and EPMA analyses revealed that the black material on the surfaces of the Mesopotamian clay tablets is mainly composed of manganese. As XRD peaks attributable to manganese minerals were not obtained from all samples by micro-XRD analysis, it seems that the manganese-bearing material is mainly present as amor-
phous manganese oxide or hydroxide. However, XRD peaks identifiable as buserite were obtained from some samples. Additionally, under the FE-SEM, rod-shaped bacteria (bacilli)-like materials with a length of 100 - 200 nm and a width of 30 nm were seen, which were gathered and changed into platy crystals. These facts may suggest that the blackening phenomena on the surfaces of the clay tablets were caused by the action of manganese-oxidizing microbe. Oxidation and concentration of manganese by microbial activity are also seen in manganese nodules and crusts on the sea floor and in desert varnish on the rock surface (Dorn & Oberlander, 1981; Perry & Adams, 1978; Potter & Rossman, 1977; Wang et al., 2011). Similar phenomena of manganese concentration by the microbial activity are observed in caves and the bottoms of rivers (Kanai et al., 2006). Concentration of manganese or iron by microbial activity is frequently seen in the natural world. However, the size of manganese-oxidizing microbe-like materials observed in this study by FE-SEM is one order of magnitude smaller than the manganese-oxidizing microbe found in manganese nodules and desert varnish reported previously (Wang & Müller, 2009; Dorn & Oberlander, 1981; Wang et al., 2011). To characterize and identify the microbe-like materials seen in the clay tablets, DNA analysis (16S rDNA) will be indispensable in future studies in spite of difficulty in collecting the sufficient amount of sample.

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