# APPENDIX 5.1: X-RAY FLUORESCENCE (XRF) MEASUREMENTS OF RED INK ON A TEL MALḤATA OSTRACON

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The dominant elemental components of the red ink on an ostracon from Tel Malḥata (Reg. No. 1071/1; Chapter 5, Inscription No. 9), were analyzed using non-destructive X-ray fluorescence spectroscopy (XRF). XRF analysis was also employed to identify chemical elements present in black and red inks of the Dead Sea manuscripts from Qumran (Nir-El and Broshi 1996a–b). It was demonstrated that the black ink did not show the presence of iron-gall (Nir-El and Broshi 1996a), and therefore it was presumed to be based on a carbonaceous pigment, even though the very low energy Carbon K absorption edge (283 eV, below detection threshold) could not be explicitly observed. The XRF analyses showed that the red ink was based on mercuric sulfide (HgS), usually known as cinnabar (Nir-El and Broshi 1996b). Pigments in the Book of the Dead (Di Stefano and Fuchs 2011; Jenkins 2011) were also analyzed using XRF. The researchers determined that the black ink was most likely based on carbon, while the red ink was most likely based on red iron oxide.

Most ancient documents were written with black ink. Red ink was used in antiquity mainly to write rubrics, that is, words at the beginning of a chapter or at paragraph divisions, titles, or instructions for liturgical readings. The most abundant surviving Iron Age II Hebrew texts (from the Kingdoms of Israel and Judah), are inscriptions written with black ink on clay potsherds (ostraca). Texts from this period written with black ink on papyrus have rarely survived. Tel Malḥata Inscription No. 9 is a very rare example of a surviving ostracon that was written with red ink. Our analysis revealed that this red ink contains iron, and is therefore very likely based on dark red ferric oxide, $Fe_2O_3$ (hematite). It does not contain Hg, Pb or As; it is not based on cinnabar, lead oxides or arsenic sulfide. It differs from the mercuric sulfide red ink used later in the Qumran Dead Sea Scrolls. Below, we describe the equipment, measurements and conclusions of this study.

## EQUIPMENT

The XRF analyses were carried out using a commercial portable XRF Silicon Drift detector (SDD-pXRF) apparatus made by Thermo Scientific. The model is Niton XLt-900 GOLDD equipped with a 50 kV X-ray tube with a Geometrically Optimized Large Area silicon Drift Detector (GOLDD), 80 MHz real-time digital signal processing, and dual embedded processors for computation and data storage. The irradiation area was a circular, 8 mm diameter spot, centered on the ostracon ink. The pXRF analyzer determines which elements are present in the sample and their relative concentrations. Using the so-called "mining" matrix, analysis is carried out for 35 chemical elements ranging from Mg (Z = 12) to Bi (Z = 83).

## MEASUREMENTS

The measurements were conducted at the Laboratory for Comparative Microarchaeology (headed by Yuval Goren) at Tel Aviv University during 2011 (Table 5.1). They were made on two different spots of ink ("Red Ink 1," "Red Ink 2") and on a clay surface without red ink ("Blank"). The measurements were repeated in pairs (1–2, 3–4, 5–6). As a check on the iron results, we also made measurements on spectroscopically pure, fine red powder $Fe_2O_3$ (hematite; "Powder"), and steel chips ("Chips") sampled from a steel plate (ca. 1940) having iron (Fe) and manganese (Mn) concentrations of ~99.5% and ~0.4% respectively.

Results were obtained for the elemental mass concentrations in percentages. Uncertainties are given at the 2σ 95% confidence level. Weighted averages and 2σ uncertainties are reported below as $x_i \pm u_i$.

## RESULTS AND DISCUSSION

### *RED INK*

#### Iron

Analysis of the iron data gives the results shown in Table 5.2, where *x* is the weighted average and *u* is the uncertainty. The iron concentration at the two red ink spots is similar (4.464 ± 0.018, 4.469 ± 0.025 %). The difference between the iron concentration in ink versus clay regions is 0.215±0.023 %; i.e., much larger than the 2σ measurement uncertainty. Data that we label "Ink" actually also contain ceramic (Blank) data, since the 8 mm diameter X-ray spot size is larger than the typical ink width (~3 mm), and the very thin ink thickness hardly attenuates X-rays coming from the underlying ceramics. The net results given above (Ink-Blank) remove the ceramics contributions sufficiently well, so that the resulting elemental analysis corresponds to the pure ink composition.

TABLE 5.1: XRF MEASUREMENTS OF INSCRIPTION NO. 9 AND ASSOCIATED ITEMS

| *Meas. #* | *Counting time (s)* | *Item* | *Sample* |
|---|---|---|---|
| 1-2 | 240 | Ostracon | Red Ink 1 |
| 3-4 | 240 | Ostracon | Blank |
| 5-6 | 240 | Ostracon | Red Ink 2 |
| 7 | 240 | $Fe_2O_3$ | Powder |
| 8 | 240 | Steel | Chips |

TABLE 5.2: CONCENTRATIONS AND UNCERTAINTIES (IN %) FOR IRON

| *Meas. #* | *Sample* | *x (%)* | *u (%)* |
|---|---|---|---|
| 1 | Red Ink | 4.461 | 0.025 |
| 2 | Red Ink | 4.466 | 0.025 |
| 1-2 | Wt average | 4.464 | 0.018 |
| 3 | Blank | 4.248 | 0.025 |
| 4 | Blank | 4.252 | 0.025 |
| 3-4 | Wt average | 4.251 | 0.018 |
| 5 | Red Ink | 4.452 | 0.025 |
| 6 | Red Ink | 4.487 | 0.026 |
| 5-6 | Wt average | 4.469 | 0.025 |
| 1-2, 5-6 | Wt average | 4.466 | 0.014 |

Data on the $Fe_2O_3$ and steel samples verifies that iron is identified at a high level of accuracy. All of these measurements constitute high-confidence proof that the red ink contains iron. The red ink on Inscription No. 9 is most likely based on red ferric oxide $Fe_2O_3$ (hematite).

The concentrations of other potential components of the red ink [arsenic (As), mercury (Hg), lead (Pb)] are much lower than the level of detection, and their uncertainties are very large. Hence, this ink is not made of arsenic sulfide (AsS, realgar), lead oxide (litharge, PbO; and minium $Pb_3O_4$), or mercuric sulfide (HgS, cinnabar).

### Other Elements

Measured concentrations of other elements, higher than 0.4%, are shown in Table 5.3. The concentrations of aluminum (Al), potassium (K) and silicon (Si) in the red ink are higher than in the clay. The concentration of calcium (Ca) in the blank is higher than in the red ink. Therefore, the red ink contains aluminum, silicon and potassium, but not calcium. It is known that antique prescriptions for red ink include the pigment $Fe_2O_3$ as the principal color-producing ingredient, as well as a clay base (for softness and texture) originating from silicate rocks. Such rocks commonly contain aluminum, potassium and silicon.

TABLE 5.3: CONCENTRATIONS AND UNCERTAINTIES (IN %) OF OTHER ELEMENTS

| # | *Sample* | *Al* | *u (Al)* | *Si* | *u (Si)* | *K* | *u (K)* | *Ca* | *u (Ca)* | *Ti* | *u (Ti)* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Red Ink | 0.972 | 0.042 | 8.696 | 0.065 | 2.263 | 0.027 | 7.311 | 0.039 | 0.445 | 0.005 |
| 2 | Red Ink | 1.043 | 0.042 | 8.575 | 0.065 | 2.236 | 0.027 | 7.310 | 0.040 | 0.452 | 0.005 |
| 3 | Blank | 0.955 | 0.042 | 8.505 | 0.066 | 1.631 | 0.023 | 8.239 | 0.042 | 0.463 | 0.005 |
| 4 | Blank | 0.956 | 0.042 | 8.403 | 0.065 | 1.580 | 0.023 | 8.133 | 0.041 | 0.461 | 0.005 |
| 5 | Red Ink | 1.102 | 0.044 | 8.629 | 0.067 | 2.766 | 0.030 | 6.431 | 0.037 | 0.425 | 0.005 |
| 6 | Red Ink | 1.078 | 0.044 | 8.808 | 0.067 | 2.733 | 0.030 | 6.418 | 0.038 | 0.428 | 0.005 |

### *BLACK INK*

We also carried out an XRF analysis of black ink on Tel Malḥata Inscription No. 4A (Reg. No. 4189/1). The analysis could not explicitly identify carbon, since its characteristic X-ray energy is far below the detection threshold. We found that the net concentration of iron (Fe) in the black ink of this ostracon is consistent with zero. The black ink is thus not iron-based like iron-gall, and is most likely lampblack or soot.

## CONCLUSIONS

We determined that the red ink in Inscription No. 9 does not contain Hg, Pb or As; it is not based on cinnabar or lead oxides or arsenic sulfide. It contains iron as the coloring component and is most likely based on the pigment ferric oxide, $Fe_2O_{3.}$ (hematite). This red ink differs from the mercuric sulfide, HgS (cinnabar) red ink used in the Qumran Dead Sea Scrolls.

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