Inventing Metallurgy in western Eurasia: a look through the microscope lens

Supplementary Materials

# **Methods**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **No.** | **Analytical No.** | **Type of Material** | **OM** | **SEM-EDS** |
| 1 | **Lepenski Vir 1** | Copper mineral | X | X |
| 2 | **Vlasac 2a** | Copper mineral | X | X |
| 3 | **Kolubara-Jariciste S16** | Copper mineral | X | X |
| 4 | **Belovode 3** | Copper mineral | X | X |
| 5 | **Belovode M20** | Copper slag | X | X |
| 6 | **Belovode M21** | Copper slag | X | X |
| 7,8 | **Belovode M22 (a, b)** | Copper slag | XX | XX |
| 9 | **Belovode M23** | Copper slag | X | X |
| 10, 11 | **Belovode 30a, 30c** | Slagged ceramic sherd | XX | XX |
| 12, 13 | **Belovode 31a, 31b** | Slagged ceramic sherd | XX | XX |
| 14 | **Belovode 33b** | Copper mineral | X | X |
| 15 | **Belovode 34a** | Copper minerals | XXX | XXX |
| 16 | **Belovode 131** | Copper slag | X | X |
| 17 | **Belovode 134** | Copper slag | X | X |
| 18 | **Belovode 136** | Copper slag | X | X |
| 19 | **Belovode M6** | Copper metal droplet | X | X |
| 20 | **Belovode M10** | Copper mineral | X | X |
| 21 | **Vinča 79** | Copper slag | X | X |
| 22 | **Vinča 91** | Copper slag | X | X |
| 23 | **Vinča 99** | Copper mineral | X | X |
| 24 | **Pločnik 51** | Copper mineral | X | X |
| 25 | **Pločnik 52** | Copper metal droplet | X | X |
| 26 | **Pločnik 54m** | Copper mineral | X | X |
| 27 | **Pločnik 57** | Copper mineral | X | X |
| 28 | **Pločnik 72m** | Copper mineral | X | X |
| 29 | **Pločnik 209** | Copper mineral | X | X |
| 30 | **Gornja Tuzla 182a** | Slagged ceramic sherd | X | X |

Table S1. Analytical techniques applied on the studied assemblage.

All samples were cut to size, mounted in epoxy resin discs, ground using abrasive disks (1200 and 2400 grit) and polished using diamond pastes (1 μm and ¼ μm). They were examined by reflected light microscopy (OM, Leica DMLM and Olympus BX60) prior to Scanning Electron Microscopy with Energy Dispersive Spectrometry (Philips XL30ESEM, Superprobe JEOL-JXA-8600) investigation. SEM-EDS used an accelerating voltage of 20 kV, with average dead-time of 35–40 % and working distance of 10 mm. All data are presented as normalized with stoichiometrically added oxygen, if not otherwise stated. The iron content is presented as FeO, which here stands for total iron (both valencies).

# **Results**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | MgO | Al2O3 | SiO2 | P2O5 | K2O | CaO | MnO | FeO | CoO | NiO | CuO | ZnO | As2O3 | BaO | PbO |
|  | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| Lepenski Vir 1 | 0.0 | 13.0 | 13.1 | 1.5 | 0.0 | 2.4 | 31.4 | 0.6 | 0.0 | 0.0 | 37.3 | 0.7 | 0.0 | 0.0 | 0.0 |
| Vlasac 2a | 0.0 | 10.3 | 12.0 | 1.8 | 0.1 | 2.0 | 32.9 | 1.0 | 0.0 | 0.0 | 39.0 | 1.0 | 0.0 | 0.0 | 0.0 |
| Kolubara S16 | 0.1 | 7.9 | 24.2 | 2.1 | 0.0 | 1.8 | 20.3 | 0.5 | 0.0 | 0.0 | 39.0 | 4.1 | 0.0 | 0.0 | 0.0 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Belovode M10 | 0.0 | 1.8 | 3.3 | 0.6 | 0.0 | 0.3 | 56.5 | 1.7 | 0.0 | 0.0 | 9.4 | 1.5 | 0.0 | 0.0 | 24.7 |
| Belovode 34a | 0.5 | 8.5 | 6.2 | 1.3 | 0.0 | 0.7 | 25.7 | 0.7 | 0.0 | 0.0 | 55.9 | 0.6 | 0.0 | 0.0 | 0.0 |
| Pločnik 51 | 0.3 | 3.6 | 13.4 | 2.1 | 0.2 | 3.1 | 29.0 | 18.6 | 0.1 | 0.0 | 26.6 | 1.7 | 0.0 | 0.0 | 1.4 |
| Pločnik 54m | 0.0 | 3.6 | 22.0 | 0.9 | 0.0 | 2.5 | 28.5 | 0.8 | 0.0 | 0.0 | 40.1 | 1.5 | 0.0 | 0.0 | 0.0 |
| Pločnik 57 | 0.1 | 1.5 | 9.0 | 1.6 | 0.0 | 2.2 | 44.3 | 0.0 | 0.0 | 0.0 | 41.4 | 0.0 | 0.0 | 0.0 | 0.0 |
| Pločnik 209 | 0.0 | 1.0 | 7.5 | 1.9 | 0.0 | 1.5 | 17.5 | 53.1 | 0.3 | 0.0 | 13.8 | 3.3 | 0.0 | 0.0 | 0.0 |
| Vinča 99 | 0.3 | 3.1 | 23.4 | 0.1 | 0.1 | 2.5 | 30.3 | 0.4 | 3.4 | 0.2 | 35.4 | 0.5 | 0.2 | 0.2 | 0.0 |

Table S2. SEM-EDS compositional data for oolithic structures in minerals, given in wt%. The fine line separates the Early Neolithic from the Vinča culture sites. All values are given as averages of 2–13 analyses of each sample.