

# Invasive and Non-invasive Analyses of Ochre and Iron-based Pigment Raw Materials: A Methodological Perspective

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**Table S1.** EDXS data compared with ICP-OES (major) data for 5 geologic samples (powder pellets). Contents in major elements were normalised to 100% by using a conventional list of elements (ICP-OES data). The relative difference (ICP-OES data used as references) is higher than 10% for the three major elements Si, Fe, Al when their concentration is higher than 6%, and higher than 25% when lower.

| Oxid<br>e                      | 14043a          |        |                    |       | 14050b          |        |                    |       | 14696c          |        |                    |       | 14697a          |        |                    |       | 14699a          |        |                    |       |
|--------------------------------|-----------------|--------|--------------------|-------|-----------------|--------|--------------------|-------|-----------------|--------|--------------------|-------|-----------------|--------|--------------------|-------|-----------------|--------|--------------------|-------|
|                                | EDXS<br>AV<br>G | S<br>D | ICP-OES<br>AV<br>G | SD    | EDXS<br>AV<br>G | S<br>D | ICP-OES<br>AV<br>G | SD    | EDXS<br>AV<br>G | S<br>D | ICP-OES<br>AV<br>G | SD    | EDXS<br>AV<br>G | S<br>D | ICP-OES<br>AV<br>G | SD    | EDXS<br>AV<br>G | S<br>D | ICP-OES<br>AV<br>G | SD    |
| SiO <sub>2</sub>               | 55.9            | 0.6    | 55.6               | 0.6   | 46.5            | 0.1    | 46.6               | 0.5   | 55.8            | 0.3    | 58.0               | 0.5   | 2.5             | 0.1    | 2.0                | 2.6   | 17.7            | 0.2    | 17.5               | 0.2   |
| Al <sub>2</sub> O <sub>3</sub> | 25.0            | 0.2    | 25.5               | 0.3   | 26.2            | 0.1    | 26.3               | 0.3   | 27.0            | 0.3    | 26.5               | 0.2   | 4.0             | 0.4    | 3.4                | 0.1   | 17.7            | 0.2    | 17.2               | 0.9   |
| Fe <sub>2</sub> O <sub>3</sub> | 11.0            | 0.3    | 10.9               | 0.2   | 16.7            | 0.1    | 17.0               | 0.3   | 6.0             | 0.2    | 5.1                | 0.1   | 89.7            | 0.4    | 91.5               | 1.8   | 60.4            | 0.4    | 61.8               | 1.2   |
| MnO                            | nd              | -      | 0.062              | 0.003 | 0.1             | 0.1    | 0.113              | 0.006 | nd              | -      | 0.003              | 0.001 | nd              | -      | 0.020              | 0.001 | nd              | -      | 0.008              | 0.001 |
| MgO                            | 0.9             | 0.1    | 0.8                | 0.1   | 1.2             | 0.1    | 1.0                | 0.1   | 2.1             | 0.2    | 1.8                | 0.1   | 0.5             | 0.1    | 0.3                | 0.1   | 0.2             | 0.1    | 0.2                | 0.1   |
| CaO                            | 0.1             | 0.1    | <L.D.              | -     | 0.3             | 0.1    | <L.D.              | -     | 0.1             | 0.1    | 0.0                | -     | 0.2             | 0.1    | 0.2                | -     | nd              | -      | <L.D.              | -     |
| Na <sub>2</sub> O              | 0.5             | 0.1    | 0.4                | 0.1   | 0.8             | 0.1    | 0.4                | 0.1   | 2.4             | 0.3    | 2.0                | -     | 0.4             | 0.1    | 0.2                | -     | 0.2             | 0.1    | <L.D.              | -     |
| K <sub>2</sub> O               | 5.0             | 0.1    | 5.1                | 0.1   | 6.3             | 0.1    | 6.4                | 0.1   | 5.7             | 0.1    | 5.4                | 0.1   | 0.1             | 0.1    | 0.1                | -     | 0.4             | 0.1    | 0.4                | 0.1   |
| TiO <sub>2</sub>               | 1.1             | 0.1    | 1.4                | 0.1   | 1.3             | 0.1    | 1.7                | 0.1   | 1.0             | 0.1    | 1.1                | 0.1   | 0.0             | nd     | -                  | -     | 0.1             | 0.1    | 0.1                | 0.1   |
| P <sub>2</sub> O <sub>5</sub>  | 0.4             | 0.1    | 0.3                | 0.1   | 0.5             | 0.1    | 0.3                | 0.1   | 0.0             | 0.1    | 0.1                | -     | 2.5             | 0.1    | 2.1                | -     | 3.3             | 0.1    | 2.8                | 0.3   |
| <b>Total</b>                   | 100.0           | -      | 100.0              | -     | 100.0           | -      | 100.0              | -     | 100.0           | -      | 100.0              | -     | 100.0           | -      | 100.0              | -     | 100.0           | -      | 100.0              | -     |

AVG : average ; SD : standard deviation ; nd :not detected ; L.D.: detection limit.

**Table S2.** Comparison of PIXE data with ICP-OES (major) and ICP-MS (traces) results for 5 geologic samples (powder pellets). Contents in major elements were normalised to 100% by using a conventional list of elements (ICP-OES data). The relative difference was calculated by using ICP values as references. In red: relative diff. >10% for major elements; >25% for trace elements.

| Ox-<br>ide/element             | ICP | 14043a    |                   |         | 14050b   |                   |         | 14696c   |                   |         | 14697a   |                   |        | 14699a    |                   |        |
|--------------------------------|-----|-----------|-------------------|---------|----------|-------------------|---------|----------|-------------------|---------|----------|-------------------|--------|-----------|-------------------|--------|
|                                |     | PIX<br>E  | Relative<br>Diff. | IC<br>P | PIX<br>E | Relative<br>Diff. | IC<br>P | PIX<br>E | Relative<br>Diff. | IC<br>P | PIX<br>E | Relative<br>Diff. | ICP    | PIX<br>E  | Relative<br>Diff. |        |
| SiO <sub>2</sub>               | %   | 55.6      | 54.6              | 1.7     | 46.6     | 46.8              | −0.5    | 58.0     | 56.5              | 2.7     | 2.0      | 2.2               | −8.8   | 17.5      | 18.4              | −5.5   |
| Al <sub>2</sub> O <sub>3</sub> | %   | 25.5      | 26.9              | −5.6    | 26.3     | 26.5              | −0.7    | 26.5     | 28.5              | −7.4    | 3.4      | 3.7               | −9.7   | 17.2      | 18.3              | −6.3   |
| Fe <sub>2</sub> O <sub>3</sub> | %   | 10.9      | 10.6              | 3.1     | 17.0     | 16.8              | 1.5     | 5.1      | 5.0               | 2.6     | 91.5     | 91.3              | 0.2    | 61.8      | 60.1              | 2.7    |
| MnO*                           | %   | 0.1       | 0.1               | 6.8     | 0.1      | 0.1               | 16.4    | 0.0<br>1 | nd                | -       | 0.0<br>1 | n.d.              | -      | 0.01      | nd                | -      |
| MgO                            | %   | 0.8       | 0.7               | 8.9     | 1.0      | 0.9               | 10.9    | 1.8      | 1.5               | 16.3    | 0.3      | 0.3               | 1.6    | 0.2       | 0.2               | 18.6   |
| CaO                            | %   | <L.<br>D. | 0.1               | -       | 0.2      | 0.3               | −49.0   | 0.0      | 0.1               | −78.7   | 0.2      | 0.2               | 24.6   | <L.<br>D. | 0.0               | -      |
| Na <sub>2</sub> O              | %   | 0.4       | 0.4               | −0.7    | 0.4      | 0.5               | −12.6   | 2.0      | 1.9               | 3.3     | 0.2      | 0.3               | −59.0  | <L.<br>D. | 0.1               | -      |
| K <sub>2</sub> O               | %   | 5.1       | 5.0               | 2.2     | 6.4      | 6.1               | 3.3     | 5.4      | 5.5               | −2.0    | 0.1      | 0.1               | −0.1   | 0.4       | 0.4               | 6.2    |
| TiO <sub>2</sub>               | %   | 1.4       | 1.4               | −1.0    | 1.7      | 1.7               | −2.2    | 1.1      | 1.1               | −0.3    | 0.0      | 0.0               | 6.0    | 0.1       | 0.1               | 25.3   |
| P <sub>2</sub> O <sub>5</sub>  | %   | 0.3       | 0.3               | 10.4    | 0.3      | 0.3               | 9.6     | 0.1      | nd                | -       | 2.1      | 1.8               | 14.3   | 2.8       | 2.4               | 12.8   |
| Total                          | %   | 100.0     | 100.0             | -       | 100.0    | 100.0             | -       | 100.0    | 100.0             | -       | 100.0    | 100.0             | -      | 100.0     | 100.0             | -      |
| As                             | ppm | 40.8      | 39.3              | 3.6     | 85.3     | 80.7              | 5.4     | 1.6      | nd                | -       | 36.2     | 35.0              | 3.4    | 41.8      | 39.3              | 5.9    |
| Ba                             | ppm | 618.2     | 660.3             | −6.8    | 738.8    | 608.3             | 17.7    | 648.3    | 598.7             | 7.7     | 437.2    | 441.0             | −0.9   | 52.5      | nd                | -      |
| Cr                             | ppm | 105.2     | 71.0              | 32.5    | 171.7    | 130.3             | 24.1    | 96.53    | 109.0             | −12.9   | 21.67    | nd                | -      | 102.7     | 98.0              | 4.6    |
| Cu                             | ppm | 32.5      | 19.0              | 41.6    | 24.3     | 17.0              | 30.0    | 8.3      | 11.3              | −36.1   | 15.2     | 19.3              | −27.1  | 56.7      | 45.0              | 20.7   |
| Ga                             | ppm | 39.7      | 31.7              | 20.3    | 45.4     | 37.0              | 18.6    | 34.0     | 26.7              | 21.6    | 1.7      | 5.0               | −190.9 | 3.8       | 4.5               | −16.9  |
| Nb                             | ppm | 25.1      | 25.3              | −1.0    | 29.9     | 34.3              | −14.7   | 18.2     | 17.0              | 6.5     | 0.5      | nd                | -      | 1.1       | nd                | -      |
| Ni                             | ppm | 25.7      | 36.0              | −39.9   | 22.5     | 32.3              | −43.8   | 9.8      | 27.7              | −181.0  | 32.5     | 60.3              | −85.9  | 27.7      | 25.7              | 7.4    |
| Pb                             | ppm | 52.3      | 49.7              | 5.0     | 70.9     | 67.3              | 5.1     | 7.9      | 8.5               | −7.7    | 5.8      | nd                | -      | 30.3      | 25.0              | 17.6   |
| Rb                             | ppm | 184.7     | 183.0             | 0.9     | 221.8    | 232.0             | −4.6    | 279.8    | 291.0             | −4.0    | 5.0      | 5.0               | −1.0   | 14.9      | 12.7              | 15.2   |
| Sr                             | ppm | 151.6     | 147.0             | 3.0     | 194.7    | 201.3             | −3.4    | 67.7     | 69.7              | −3.0    | 47.3     | 55.0              | −16.2  | 6.6       | 8.0               | −21.4  |
| Th                             | ppm | 25.1      | 21.7              | 13.6    | 27.9     | 26.7              | 4.4     | 28.0     | 24.7              | 11.7    | 7.5      | nd                | -      | 3.0       | nd                | -      |
| V                              | ppm | 102.6     | 169.5             | −65.2   | 138.4    | 215.0             | −55.3   | 101.0    | nd                | -       | 6.9      | nd                | -      | 15.9      | 35.5              | −122.7 |
| Y                              | ppm | 57.4      | 50.0              | 12.9    | 71.2     | 73.7              | −3.5    | 38.9     | 36.7              | 5.8     | 6.6      | 5.0               | 23.7   | 7.2       | 6.0               | 16.9   |
| Zr                             | ppm | 476.7     | 438.7             | 8.0     | 338.6    | 333.7             | 1.5     | 207.5    | 204.0             | 1.7     | 16.7     | 18.0              | −7.7   | 16.4      | 16.3              | 0.2    |
| Zn                             | ppm | 70.5      | 48.0              | 30.9    | 83.0     | 64.0              | 23.4    | 56.0     | 38.0              | 32.3    | 24.0     | 25.0              | −2.3   | 55.1      | 39.0              | 28.6   |

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*Diff.: difference; nd: not detected.*

**Table S3.** Detailed results of SEM-EDXS analyses of archaeological samples (surface and section).

| Sample           | Mode    | Analysis  | Na <sub>2</sub> O | MgO | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | S   | Cl | K <sub>2</sub> O | CaO | TiO <sub>2</sub> | V <sub>2</sub> O <sub>5</sub> | MnO | Fe <sub>2</sub> O <sub>3</sub> | ZrO | Total |
|------------------|---------|-----------|-------------------|-----|--------------------------------|------------------|-------------------------------|-----|----|------------------|-----|------------------|-------------------------------|-----|--------------------------------|-----|-------|
| 13681<br>(shale) | Surface | AVERAGE   | 1.2               | 2.1 | 20.6                           | 52.4             | 4.5                           | 1.9 | nd | 5.5              | 1.9 | 1.0              | nd                            | 0.1 | 9.4                            | 0.1 | 99.6  |
|                  |         | SD        | 0.4               | 0.3 | 1.8                            | 5.8              | 2.5                           | 1.6 | -  | 0.7              | 0.4 | 0.2              | -                             | 0.1 | 5.1                            | 0.3 | -     |
|                  | Section | 1 (edge)  | 0.3               | 0.7 | 18.5                           | 69.6             | 1.1                           | nd  | nd | 3.7              | 0.5 | 0.9              | nd                            | nd  | 4.5                            | nd  | 99.8  |
|                  |         | 2         | 0.3               | 0.8 | 19.9                           | 66.6             | 1.2                           | nd  | nd | 4                | 0.4 | 1.2              | nd                            | nd  | 5.2                            | nd  | 99.8  |
|                  |         | 3         | 0.3               | 0.8 | 20                             | 67.2             | 1.1                           | nd  | nd | 4.3              | 0.4 | 0.9              | nd                            | nd  | 4.7                            | nd  | 99.8  |
|                  |         | 4         | 0.3               | 0.8 | 19.6                           | 68.2             | 1                             | nd  | nd | 4                | 0.4 | 0.8              | nd                            | nd  | 4.7                            | nd  | 99.8  |
|                  |         | 5         | 0.4               | 0.9 | 19                             | 67               | 1.2                           | nd  | nd | 4.4              | 0.4 | 1.4              | nd                            | nd  | 5.3                            | nd  | 99.8  |
|                  |         | 6         | 0.5               | 1.1 | 21.8                           | 61.9             | 1.3                           | nd  | nd | 5.1              | 0.4 | 1.3              | nd                            | nd  | 5.9                            | 0.6 | 99.7  |
|                  |         | 7         | 0.3               | 0.7 | 20.1                           | 68.4             | 0.8                           | nd  | nd | 4.1              | 0.2 | 0.6              | nd                            | nd  | 4.7                            | nd  | 99.8  |
|                  |         | 8         | 0.3               | 0.7 | 21.6                           | 66.5             | 1.1                           | nd  | nd | 4.1              | 0.3 | 0.9              | nd                            | nd  | 4.3                            | nd  | 99.7  |
|                  |         | 9         | 0.2               | 0.4 | 15.8                           | 76.4             | 0.5                           | nd  | nd | 2.2              | 0.2 | 1                | nd                            | nd  | 3.2                            | nd  | 99.8  |
|                  |         | 10        | 0.4               | 0.9 | 20.4                           | 65               | 1.4                           | nd  | nd | 4.7              | 0.4 | 1                | nd                            | nd  | 5.1                            | 0.4 | 99.7  |
|                  |         | 11        | 0.3               | 0.8 | 18.1                           | 70.7             | 1.3                           | nd  | nd | 3.4              | 0.4 | 0.8              | nd                            | nd  | 3.8                            | nd  | 99.6  |
|                  |         | 12 (edge) | 0.3               | 0.7 | 19.2                           | 69               | 1.5                           | nd  | nd | 3.1              | 0.4 | 1.6              | nd                            | nd  | 3.6                            | nd  | 99.6  |
|                  |         | AVERAGE   | 0.3               | 0.8 | 19.5                           | 68.0             | 1.1                           | -   | -  | 3.9              | 0.4 | 1.0              | -                             | -   | 4.6                            | 0.1 | 99.7  |
|                  |         | SD        | 0.1               | 0.2 | 1.6                            | 3.5              | 0.3                           | -   | -  | 0.8              | 0.1 | 0.3              | -                             | -   | 0.8                            | 0.2 | -     |
|                  |         | MAX       | 0.5               | 1.1 | 21.8                           | 76.4             | 1.4                           | -   | -  | 5.1              | 0.5 | 1.4              | -                             | -   | 5.9                            | 0.6 | -     |
|                  |         | MIN       | 0.2               | 0.4 | 15.8                           | 61.9             | 0.5                           | -   | -  | 2.2              | 0.2 | 0.6              | -                             | -   | 3.2                            | nd  | -     |
| 13690<br>(ferr)  | surface | AVERAGE   | 3.4               | 3.1 | 4.2                            | 16.3             | 0.5                           | 0.2 | nd | 3.2              | 0.6 | 0.6              | nd                            | nd  | 66.9                           | nd  | 98.9  |
|                  |         | SD        | 1.2               | 1.2 | 1.1                            | 3.6              | 0.2                           | 0.1 | -  | 1.0              | 0.2 | 0.2              | -                             | -   | 7.1                            | -   | -     |
|                  | section | 1 (edge)  | 0.5               | 1.4 | 5.1                            | 26.2             | 0.2                           | nd  | nd | 1.8              | 0.1 | 1.0              | 0.1                           | nd  | 63.1                           | nd  | 99.5  |
|                  |         | 2         | 0.5               | 1.2 | 4.9                            | 24.0             | 0.2                           | nd  | nd | 1.7              | 0.1 | 0.8              | nd                            | nd  | 66.2                           | nd  | 99.5  |
|                  |         | 3         | 0.4               | 1.0 | 4.7                            | 26.7             | 0.2                           | nd  | nd | 1.5              | 0.1 | 0.6              | 0.2                           | nd  | 64.1                           | nd  | 99.5  |
|                  |         | 4         | 0.4               | 1.0 | 4.9                            | 24.4             | 0.2                           | nd  | nd | 1.5              | 0.1 | 0.7              | 0.1                           | nd  | 66.1                           | nd  | 99.5  |
|                  |         | 5         | 0.5               | 1.0 | 5.1                            | 24.9             | 0.2                           | nd  | nd | 1.5              | 0.1 | 0.7              | nd                            | nd  | 65.4                           | nd  | 99.5  |
|                  |         | 6         | 0.5               | 1.3 | 5.8                            | 22.5             | nd                            | nd  | nd | 1.4              | 0.1 | 0.6              | 0.1                           | nd  | 66.9                           | nd  | 99.4  |
|                  |         | 7         | 0.5               | 1.1 | 4.9                            | 22.5             | 0.2                           | nd  | nd | 1.3              | nd  | 0.6              | 0.1                           | nd  | 68.2                           | nd  | 99.4  |
|                  |         | 8         | 0.4               | 1.1 | 4.8                            | 22.7             | 0.2                           | nd  | nd | 1.4              | 0.1 | 0.6              | nd                            | nd  | 68.1                           | nd  | 99.4  |
|                  |         | 9         | 0.5               | 1.4 | 5.9                            | 27.3             | 0.3                           | nd  | nd | 1.7              | 0.1 | 0.7              | nd                            | nd  | 61.6                           | nd  | 99.5  |
|                  |         | 10        | 0.4               | 1.0 | 4.8                            | 30.2             | nd                            | nd  | nd | 1.4              | 0.1 | 0.7              | nd                            | nd  | 60.8                           | nd  | 99.5  |
|                  |         | 11        | 0.2               | 1.0 | 4.9                            | 32.0             | 0.2                           | nd  | nd | 1.5              | 0.1 | 0.8              | 0.2                           | nd  | 58.8                           | nd  | 99.7  |
|                  |         | 12        | 0.3               | 1.4 | 5.7                            | 30.9             | 0.3                           | nd  | nd | 1.6              | 0.1 | 0.8              | 0.1                           | nd  | 58.5                           | nd  | 99.6  |
|                  |         | 13 (edge) | 0.3               | 1.2 | 5.0                            | 28.8             | 0.3                           | nd  | nd | 1.6              | 0.1 | 0.8              | nd                            | nd  | 61.6                           | nd  | 99.7  |
|                  |         | 14 (edge) | 0.4               | 1.1 | 4.7                            | 27.5             | nd                            | nd  | nd | 1.4              | 0.1 | 0.7              | 0.2                           | nd  | 63.5                           | nd  | 99.7  |
|                  |         | AVERAGE   | 0.4               | 1.2 | 5.1                            | 26.5             | 0.2                           | -   | -  | 1.5              | 0.1 | 0.7              | 0.1                           | -   | 63.8                           | -   | 99.5  |
|                  |         | SD        | 0.1               | 0.2 | 0.4                            | 3.2              | 0.1                           | -   | -  | 0.1              | 0.0 | 0.1              | 0.1                           | -   | 3.2                            | -   | -     |
|                  |         | MAX       | 0.5               | 1.4 | 5.9                            | 32.0             | 0.3                           | -   | -  | 1.8              | 0.1 | 1.0              | 0.2                           | -   | 68.2                           | -   | -     |
|                  |         | MIN       | 0.2               | 1.0 | 4.7                            | 22.5             | nd                            | -   | -  | 1.3              | nd  | 0.6              | nd                            | -   | 58.5                           | -   | -     |

| Sample           | Mode    | Analysis  | Na <sub>2</sub> O | MgO | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | S   | Cl  | K <sub>2</sub> O | CaO | TiO <sub>2</sub> | V <sub>2</sub> O <sub>5</sub> | MnO | Fe <sub>2</sub> O <sub>3</sub> | ZrO | Total |
|------------------|---------|-----------|-------------------|-----|--------------------------------|------------------|-------------------------------|-----|-----|------------------|-----|------------------|-------------------------------|-----|--------------------------------|-----|-------|
| 13712<br>(shale) | Surface | AVERAGE   | 1.1               | 1.8 | 7.0                            | 9.3              | 0.8                           | 0.1 | nd  | 1.3              | 0.7 | 0.5              | nd                            | nd  | 76.6                           | nd  | 99.4  |
|                  |         | SD        | 1.0               | 0.7 | 1.4                            | 1.9              | 0.3                           | 0.1 | -   | 0.4              | 0.3 | 0.2              | -                             | -   | 5.6                            | -   | -     |
|                  | Section | 1 (edge)  | nd                | 0.5 | 7.3                            | 9.7              | 0.6                           | nd  | nd  | 1.3              | 0.4 | 0.3              | 0.8                           | nd  | 78.9                           | nd  | 99.9  |
|                  |         | 2         | 0.2               | 0.5 | 8.0                            | 10.5             | 0.4                           | nd  | nd  | 1.4              | 0.3 | 0.2              | 0.7                           | nd  | 77.6                           | nd  | 99.8  |
|                  |         | 3         | 0.3               | 0.5 | 7.4                            | 9.8              | 0.3                           | nd  | nd  | 1.4              | 0.2 | 0.3              | 0.8                           | nd  | 79.0                           | nd  | 99.9  |
|                  |         | 4         | nd                | 0.4 | 7.3                            | 10.1             | 0.3                           | nd  | nd  | 1.5              | 0.2 | 0.3              | 0.7                           | nd  | 79.0                           | nd  | 99.8  |
|                  |         | 5         | 0.2               | 0.6 | 6.5                            | 8.7              | 0.7                           | nd  | nd  | 1.4              | 0.9 | 0.3              | 0.5                           | nd  | 79.7                           | 0.3 | 99.7  |
|                  |         | 6         | 0.2               | 0.7 | 6.1                            | 8.3              | 0.9                           | nd  | nd  | 1.3              | 0.9 | 0.3              | 0.5                           | nd  | 80.6                           | nd  | 99.7  |
|                  |         | 7         | 0.1               | 0.6 | 5.6                            | 7.7              | 0.6                           | nd  | nd  | 1.2              | 0.8 | 0.3              | 0.6                           | nd  | 82.3                           | nd  | 99.8  |
|                  |         | 8         | 0.2               | 0.5 | 5.8                            | 7.6              | 0.7                           | nd  | nd  | 1.2              | 0.8 | 0.2              | 0.6                           | nd  | 82.2                           | nd  | 99.9  |
|                  |         | 9         | nd                | 0.5 | 4.8                            | 6.0              | 0.7                           | nd  | nd  | 0.9              | 0.7 | 0.4              | 0.7                           | nd  | 85.1                           | nd  | 99.9  |
|                  |         | 10        | 0.1               | 0.5 | 5.5                            | 7.0              | 0.6                           | nd  | nd  | 1.1              | 0.6 | 0.4              | 0.6                           | nd  | 83.3                           | nd  | 99.9  |
|                  |         | 11        | 0.2               | 0.5 | 6.0                            | 8.1              | 0.4                           | nd  | nd  | 1.2              | 0.3 | 0.3              | 0.7                           | nd  | 82.3                           | nd  | 99.9  |
|                  |         | 12 (edge) | 0.1               | 0.5 | 7.0                            | 9.2              | 0.4                           | nd  | nd  | 1.3              | 0.3 | 0.3              | 0.5                           | nd  | 80.2                           | nd  | 99.9  |
|                  |         | AVERAGE   | 0.1               | 0.5 | 6.4                            | 8.6              | 0.6                           | -   | -   | 1.3              | 0.5 | 0.3              | 0.6                           | -   | 80.9                           | nd  | 99.8  |
|                  |         | SD        | 0.1               | 0.1 | 1.0                            | 1.4              | 0.2                           | -   | -   | 0.2              | 0.3 | 0.1              | 0.1                           | -   | 2.2                            | 0.1 | -     |
|                  |         | MAX       | 0.3               | 0.7 | 8.0                            | 10.5             | 0.9                           | -   | -   | 1.5              | 0.9 | 0.4              | 0.8                           | -   | 85.1                           | 0.3 | -     |
|                  |         | MIN       | nd                | 0.4 | 4.8                            | 6.0              | 0.3                           | -   | -   | 0.9              | 0.2 | 0.2              | 0.5                           | -   | 77.6                           | nd  | -     |
| 13741<br>(ferr)  | Surface | AVERAGE   | 2.1               | 1.8 | 1.4                            | 2.8              | 3.5                           | 0.2 | 0.7 | 1.1              | 0.9 | nd               | nd                            | 0.3 | 85.4                           | nd  | 100.0 |
|                  |         | SD        | 0.3               | 0.4 | 0.5                            | 1.2              | 0.5                           | 0.1 | 0.1 | 0.1              | 0.3 | -                | -                             | 0.1 | 2.8                            | -   | -     |
|                  | Section | 1 (edge)  | 0.4               | 1.2 | 1.3                            | 6.0              | 2.5                           | nd  | nd  | 0.4              | 0.3 | nd               | nd                            | 0.1 | 87.5                           | nd  | 99.8  |
|                  |         | 2         | 0.4               | 0.4 | 0.8                            | 2.4              | 2.8                           | nd  | nd  | 0.3              | 0.4 | nd               | nd                            | 0.1 | 91.8                           | 0.3 | 99.8  |
|                  |         | 3         | 0.4               | 0.4 | 0.8                            | 2.3              | 2.9                           | nd  | nd  | 0.5              | 0.4 | nd               | nd                            | 0.1 | 91.9                           | nd  | 99.7  |
|                  |         | 4         | 0.4               | 0.4 | 0.8                            | 3.2              | 2.6                           | nd  | nd  | 0.4              | 0.4 | nd               | nd                            | 0.1 | 91.3                           | nd  | 99.8  |
|                  |         | 5         | 0.4               | 0.5 | 0.8                            | 3.3              | 2.8                           | nd  | nd  | 0.4              | 0.3 | nd               | nd                            | 0.1 | 91.2                           | nd  | 99.8  |
|                  |         | 6         | 0.5               | 0.4 | 0.8                            | 3.4              | 2.7                           | nd  | nd  | 0.4              | 0.4 | nd               | nd                            | 0.1 | 91.0                           | nd  | 99.8  |
|                  |         | 7         | 0.6               | 0.5 | 0.7                            | 1.3              | 2.9                           | nd  | nd  | 0.6              | 0.4 | nd               | nd                            | 0.1 | 92.7                           | nd  | 99.7  |
|                  |         | 8         | 0.6               | 0.5 | 0.8                            | 1.2              | 2.8                           | nd  | nd  | 0.5              | 0.3 | nd               | nd                            | 0.2 | 92.9                           | nd  | 99.7  |
|                  |         | 9         | 0.7               | 0.5 | 0.7                            | 1.7              | 2.8                           | nd  | nd  | 0.7              | 0.4 | nd               | nd                            | 0.2 | 91.9                           | nd  | 99.7  |
|                  |         | 10 (edge) | 0.5               | 0.6 | 0.8                            | 4.0              | 2.7                           | nd  | nd  | 0.6              | 0.4 | nd               | nd                            | 0.1 | 90.1                           | nd  | 99.7  |
|                  |         | AVERAGE   | 0.5               | 0.5 | 0.8                            | 2.9              | 2.8                           | -   | -   | 0.5              | 0.4 | -                | -                             | 0.1 | 91.2                           | 0.0 | 99.8  |
|                  |         | SD        | 0.1               | 0.2 | 0.2                            | 1.4              | 0.1                           | -   | -   | 0.1              | 0.0 | -                | -                             | 0.0 | 1.5                            | 0.1 | -     |
|                  |         | MAX       | 0.7               | 1.2 | 1.3                            | 6.0              | 2.9                           | -   | -   | 0.7              | 0.4 | -                | -                             | 0.2 | 92.9                           | 0.3 | -     |
|                  |         | MIN       | 0.4               | 0.4 | 0.7                            | 1.2              | 2.5                           | -   | -   | 0.3              | 0.3 | -                | -                             | 0.1 | 87.5                           | nd  | -     |

| Sample           | Mode    | Analysis  | Na <sub>2</sub> O | MgO | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | S   | Cl  | K <sub>2</sub> O | CaO | TiO <sub>2</sub> | V <sub>2</sub> O <sub>5</sub> | MnO | Fe <sub>2</sub> O <sub>3</sub> | ZrO | Total |
|------------------|---------|-----------|-------------------|-----|--------------------------------|------------------|-------------------------------|-----|-----|------------------|-----|------------------|-------------------------------|-----|--------------------------------|-----|-------|
| 13773<br>(shale) | Surface | AVERAGE   | 0.9               | 3.3 | 17.5                           | 40.9             | 0.6                           | 0.1 | 0.0 | 4.2              | 1.0 | 0.7              | nd                            | 0.0 | 29.2                           | nd  | 98.5  |
|                  |         | SD        | 0.5               | 0.9 | 2.0                            | 2.5              | 0.2                           | 0.1 | 0.0 | 0.5              | 0.2 | 0.1              | -                             | 0.0 | 5.2                            | -   | -     |
|                  | Section | 1 (edge)  | 0.1               | 0.8 | 13.3                           | 46.4             | 0.4                           | nd  | nd  | 3.8              | 0.1 | 0.7              | nd                            | nd  | 34.2                           | nd  | 99.8  |
|                  |         | 2         | 0.1               | 0.9 | 12.9                           | 48.6             | 0.4                           | nd  | nd  | 4.0              | 0.2 | 0.9              | nd                            | nd  | 31.8                           | nd  | 99.8  |
|                  |         | 3         | 0.2               | 1.0 | 13.4                           | 49.4             | 0.3                           | nd  | nd  | 4.3              | 0.2 | 0.7              | nd                            | nd  | 30.4                           | nd  | 99.8  |
|                  |         | 4         | 0.1               | 1.0 | 13.2                           | 48.2             | 0.4                           | nd  | nd  | 4.2              | 0.2 | 0.8              | nd                            | nd  | 31.7                           | nd  | 99.8  |
|                  |         | 5         | 0.1               | 1.0 | 13.9                           | 53.2             | 0.2                           | nd  | nd  | 4.4              | 0.1 | 0.7              | nd                            | nd  | 26.1                           | nd  | 99.8  |
|                  |         | 6         | 0.2               | 1.0 | 14.0                           | 50.2             | 0.3                           | nd  | nd  | 4.6              | 0.2 | 0.8              | nd                            | nd  | 28.5                           | nd  | 99.8  |
|                  |         | 7         | 0.2               | 1.0 | 13.9                           | 51.0             | 0.3                           | nd  | nd  | 4.5              | 0.2 | 0.8              | nd                            | nd  | 27.9                           | nd  | 99.8  |
|                  |         | 8         | 0.2               | 1.1 | 14.0                           | 52.7             | 0.3                           | nd  | nd  | 4.7              | 0.1 | 0.9              | nd                            | nd  | 25.7                           | nd  | 99.8  |
|                  |         | 9         | 0.1               | 1.0 | 13.6                           | 45.7             | 0.3                           | nd  | nd  | 4.1              | 0.2 | 0.8              | nd                            | 0.1 | 34.0                           | nd  | 99.8  |
|                  |         | 10 (edge) | 0.1               | 0.9 | 12.6                           | 48.0             | 0.3                           | nd  | nd  | 3.7              | 0.1 | 0.7              | nd                            | nd  | 33.4                           | nd  | 99.9  |
|                  |         | AVERAGE   | 0.1               | 1.0 | 13.5                           | 49.3             | 0.3                           | -   | -   | 4.2              | 0.2 | 0.8              | -                             | 0.0 | 30.4                           |     | 99.8  |
|                  |         | SD        | 0.1               | 0.1 | 0.5                            | 2.5              | 0.1                           | -   | -   | 0.3              | 0.1 | 0.1              | -                             | 0.0 | 3.2                            |     | -     |
|                  |         | MAX       | 0.2               | 1.1 | 14.0                           | 53.2             | 0.4                           | -   | -   | 4.7              | 0.2 | 0.9              | -                             | 0.1 | 34.2                           |     | -     |
|                  |         | MIN       | 0.1               | 0.8 | 12.6                           | 45.7             | 0.2                           | -   | -   | 3.7              | 0.1 | 0.7              | -                             | nd  | 25.7                           |     | -     |

Nd: not detected.

Table S4. Detailed results of PIXE analyses of archaeological samples (surface and section).

| Sample                         | Analysis         | Si<br>O <sub>2</sub><br>(%) | Al <sub>2</sub><br>O <sub>3</sub><br>(%) | Fe <sub>2</sub><br>O <sub>3</sub><br>(%) | Mn<br>O<br>(%) | Mg<br>O<br>(%) | Ca<br>O<br>(%) | Na <sub>2</sub><br>O<br>(%) | K <sub>2</sub><br>O<br>(%) | Ti<br>O <sub>2</sub><br>(%) | P <sub>2</sub><br>O <sub>5</sub><br>(%) | Total<br>(%) | As<br>PP<br>m | Ba<br>PP<br>m | Cr<br>PP<br>m | Cu<br>PP<br>m | Ga<br>PP<br>m | Nb<br>PP<br>m | Ni<br>PP<br>m | Pb<br>PP<br>m | Rb<br>PP<br>m | Sr<br>PP<br>m | V<br>PP<br>m | Y<br>PP<br>m | Zn<br>PP<br>m | Zr<br>PP<br>m |      |
|--------------------------------|------------------|-----------------------------|------------------------------------------|------------------------------------------|----------------|----------------|----------------|-----------------------------|----------------------------|-----------------------------|-----------------------------------------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|--------------|--------------|---------------|---------------|------|
| 13681<br>(shale)               | Surf             | 1                           | 54.4                                     | 24.8                                     | 7.4            | 0.05           | 1.9            | 1.0                         | 0.9                        | 5.7                         | 1.8                                     | 2.2          | 100           | 48            | 760           | 201           | 37            | 31            | 33            | 27            | 60            | 217           | 285          | nd           | 49            | 49            | 508  |
|                                |                  | 2                           | 59.4                                     | 23.2                                     | 5.1            | 0.05           | 1.9            | 1.0                         | 0.8                        | 4.7                         | 1.8                                     | 2.1          | 100           | 34            | 306           | 72            | 38            | 26            | 26            | 26            | 43            | 171           | 205          | 112          | 40            | 42            | 629  |
|                                |                  | 3                           | 54.2                                     | 24.5                                     | 7.8            | 0.05           | 1.9            | 1.0                         | 0.8                        | 5.8                         | 1.8                                     | 2.2          | 100           | 53            | 706           | 113           | 37            | 35            | 34            | 28            | 67            | 228           | 298          | 251          | 57            | 53            | 593  |
|                                |                  | AVSD                        | 56.0                                     | 24.2                                     | 6.7            | 0.05           | 1.9            | 1.0                         | 0.8                        | 5.4                         | 1.8                                     | 2.2          | 100.0         | 45            | 591           | 129           | 37            | 31            | 31            | 27            | 57            | 205           | 263          | 182          | 49            | 48            | 577  |
|                                |                  |                             | 3.0                                      | 0.8                                      | 1.5            | 0.00           | 0.0            | 0.0                         | 0.0                        | 0.6                         | 0.0                                     | 0.1          | 0.0           | 10            | 248           | 66            | 1             | 5             | 4             | 1             | 12            | 30            | 50           | 98           | 9             | 6             | 62   |
|                                | Sect             | 1                           | 63.5                                     | 22.5                                     | 5.6            | 0.02           | 1.0            | 0.3                         | 0.4                        | 4.3                         | 1.4                                     | 1.0          | 100           | 34            | 361           | 141           | 34            | 24            | 24            | 25            | 38            | 178           | 175          | 141          | 65            | 48            | 954  |
|                                |                  | 2                           | 69.6                                     | 19.9                                     | 4.2            | 0.02           | 0.7            | 0.2                         | 0.3                        | 3.2                         | 1.0                                     | 0.8          | 100           | 26            | 424           | 84            | 31            | 18            | 18            | 26            | 26            | 130           | 112          | nd           | 27            | 38            | 740  |
|                                |                  | 3                           | 64.5                                     | 22.6                                     | 4.9            | 0.03           | 0.9            | 0.3                         | 0.4                        | 4.1                         | 1.2                                     | 1.1          | 100           | 32            | 300           | 126           | 29            | 24            | 20            | 18            | 33            | 170           | 158          | 74           | 52            | 45            | 208  |
|                                |                  | 4                           | 69.5                                     | 20.4                                     | 3.6            | 0.02           | 0.7            | 0.3                         | 0.3                        | 3.2                         | 1.1                                     | 1.0          | 100           | 30            | 321           | 90            | 33            | 18            | 18            | 21            | 22            | 136           | 231          | nd           | 38            | 36            | 557  |
|                                |                  | AVSD                        | 66.7                                     | 21.4                                     | 4.6            | 0.02           | 0.9            | 0.3                         | 0.3                        | 3.7                         | 1.2                                     | 1.0          | 100.0         | 31            | 352           | 110           | 32            | 21            | 20            | 23            | 30            | 154           | 169          | 108          | 46            | 42            | 615  |
|                                |                  | 3.2                         | 1.4                                      | 0.9                                      | 0.00           | 0.1            | 0.1            | 0.1                         | 0.6                        | 0.2                         | 0.1                                     | 0.0          | 3             | 55            | 28            | 2             | 3             | 3             | 4             | 7             | 24            | 49            | 47           | 17           | 6             | 316           |      |
|                                | 13715<br>(shale) | Surf                        | 1                                        | 52.6                                     | 25.9           | 10.8           | 0.09           | 1.3                         | 0.5                        | 0.8                         | 5.8                                     | 1.8          | 0.5           | 100           | 53            | 479           | nd            | 30            | 34            | 34            | 38            | 74            | 208          | 184          | 182           | 89            | 61   |
| 2                              |                  |                             | 55.4                                     | 26.6                                     | 8.3            | 0.06           | 1.4            | 0.4                         | 0.8                        | 5.4                         | 1.3                                     | 0.3          | 100           | 35            | 655           | 94            | 27            | 26            | 23            | 22            | 59            | 157           | 136          | 88           | 34            | 48            | 291  |
| 3                              |                  |                             | 52.9                                     | 26.6                                     | 9.7            | 0.08           | 1.4            | 0.6                         | 0.9                        | 5.8                         | 1.6                                     | 0.4          | 100           | 51            | 768           | 82            | 32            | 31            | 32            | 24            | 68            | 190           | 184          | 111          | 87            | 57            | 317  |
| 4                              |                  |                             | 53.3                                     | 26.2                                     | 9.0            | 0.09           | 1.5            | 0.8                         | 1.1                        | 5.8                         | 1.4                                     | 0.8          | 100           | 48            | 798           | 104           | 33            | 30            | 27            | 30            | 56            | 182           | 162          | nd           | 47            | 62            | 415  |
| AVSD                           |                  |                             | 53.5                                     | 26.3                                     | 9.5            | 0.08           | 1.4            | 0.6                         | 0.9                        | 5.7                         | 1.5                                     | 0.5          | 100.0         | 47            | 675           | 93            | 31            | 30            | 29            | 29            | 64            | 184           | 167          | 127          | 64            | 57            | 489  |
|                                |                  | 1.2                         | 0.3                                      | 1.1                                      | 0.01           | 0.1            | 0.2            | 0.1                         | 0.2                        | 0.2                         | 0.2                                     | -            | 8             | 144           | 11            | 3             | 3             | 5             | 7             | 8             | 21            | 23            | 49           | 28           | 6             | 300           |      |
| Sect                           |                  | 1                           | 59.4                                     | 22.3                                     | 11.0           | 0.07           | 0.8            | 0.3                         | 0.4                        | 4.3                         | 1.2                                     | 0.3          | 100           | 47            | 669           | 116           | 25            | 27            | 23            | 27            | 56            | 167           | 153          | nd           | 42            | 53            | 609  |
|                                |                  | 2                           | 57.8                                     | 23.9                                     | 10.7           | 0.08           | 0.9            | 0.1                         | 0.4                        | 4.4                         | 1.6                                     | 0.2          | 100           | 46            | 692           | 99            | 23            | 27            | 28            | 22            | 49            | 169           | 165          | 133          | 77            | 51            | 352  |
|                                |                  | 3                           | 56.1                                     | 26.2                                     | 9.1            | 0.07           | 0.8            | 0.2                         | 0.3                        | 5.0                         | 1.9                                     | 0.3          | 100           | 51            | 702           | 74            | 21            | 30            | 31            | 34            | 65            | 191           | 198          | 159          | 53            | 58            | 885  |
|                                |                  | 4                           | 59.3                                     | 22.9                                     | 10.7           | 0.09           | 1.0            | 0.1                         | 0.3                        | 4.3                         | 1.2                                     | 0.2          | 100           | 51            | 594           | 76            | 26            | 28            | 23            | 34            | 57            | 163           | 142          | 218          | 37            | 51            | 379  |
|                                |                  | AVSD                        | 58.1                                     | 23.8                                     | 10.3           | 0.08           | 0.9            | 0.2                         | 0.3                        | 4.5                         | 1.4                                     | 0.3          | 100.0         | 49            | 664           | 91            | 24            | 28            | 26            | 29            | 57            | 173           | 165          | 170          | 52            | 53            | 556  |
|                                |                  | 1.5                         | 1.7                                      | 0.9                                      | 0.01           | 0.1            | 0.1            | 0.1                         | 0.3                        | 0.3                         | 0.1                                     | -            | 3             | 49            | 20            | 2             | 1             | 4             | 6             | 7             | 13            | 24            | 44           | 18           | 3             | 248           |      |
| 13716<br>(shale/<br>sandstone) | Surf             | 1                           | 40.0                                     | 8.2                                      | 43.6           | 0.01           | 1.1            | 0.8                         | 1.7                        | 2.5                         | 0.2                                     | 2.0          | 100           | 13            | 51            | 38            | 24            | 4             | 6             | 50            | 58            | 78            | 56           | nd           | 63            | 176           | 1014 |
|                                |                  | 2                           | 46.5                                     | 7.8                                      | 35.2           | 0.01           | 1.1            | 2.2                         | 2.3                        | 2.6                         | 0.3                                     | 2.1          | 100           | 10            | 92            | nd            | 22            | 5             | 4             | 44            | 55            | 70            | 56           | 38           | 12            | 202           | 33   |
|                                |                  | 3                           | 44.1                                     | 9.0                                      | 37.8           | 0.00           | 1.0            | 0.8                         | 2.0                        | 3.0                         | 0.4                                     | 2.0          | 100           | 8             | 106           | 34            | 22            | 6             | 7             | 23            | 44            | 77            | 60           | nd           | 12            | 141           | 176  |
|                                |                  | AVSD                        | 43.5                                     | 8.3                                      | 38.8           | 0.00           | 1.0            | 1.2                         | 2.0                        | 2.7                         | 0.3                                     | 2.1          | 100.0         | 10            | 83            | 36            | 23            | 5             | 6             | 39            | 52            | 75            | 57           | 38           | 29            | 173           | 408  |
|                                |                  | 3.3                         | 0.6                                      | 4.3                                      | 0.00           | 0.1            | 0.8            | 0.3                         | 0.3                        | 0.1                         | 0.1                                     | -            | 3             | 29            | 3             | 1             | 1             | 2             | 14            | 7             | 4             | 2             | nd           | 29           | 31            | 530           |      |
|                                | Sect             | 1                           | 59.4                                     | 7.7                                      | 28.9           | 0.00           | 0.5            | 0.1                         | 0.2                        | 2.3                         | 0.4                                     | 0.6          | 100           | 10            | 140           | 30            | 14            | 7             | 4             | 28            | 26            | 80            | 55           | 113          | 25            | 100           | 256  |
| 2                              |                  | 52.9                        | 5.6                                      | 38.4                                     | 0.00           | 0.3            | 0.1            | 0.2                         | 1.5                        | 0.2                         | 0.8                                     | 100          | 9             | 32            | nd            | 9             | 5             | 4             | 26            | 18            | 54            | 35            | 61           | 8            | 110           | 26            |      |

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|   |      |     |      |      |     |     |     |     |     |     |       |   |    |    |    |   |   |    |    |    |    |     |    |     |     |
|---|------|-----|------|------|-----|-----|-----|-----|-----|-----|-------|---|----|----|----|---|---|----|----|----|----|-----|----|-----|-----|
| 3 | 63.0 | 7.0 | 26.4 | 0.00 | 0.4 | 0.1 | 0.1 | 2.1 | 0.4 | 0.5 | 100   | 7 | nd | 16 | 7  | 6 | 7 | 20 | 17 | 80 | 55 | 100 | 16 | 92  | 460 |
| 4 | 57.4 | 5.4 | 34.2 | 0.00 | 0.3 | 0.1 | 0.1 | 1.6 | 0.3 | 0.6 | 100   | 7 | 94 | 47 | 9  | 5 | 5 | 30 | 22 | 65 | 33 | 36  | 11 | 111 | 47  |
| A | 58.2 | 6.4 | 31.9 | 0.00 | 0.4 | 0.1 | 0.2 | 1.9 | 0.3 | 0.6 | 100.0 | 8 | 89 | 31 | 10 | 6 | 5 | 26 | 21 | 70 | 45 | 78  | 15 | 103 | 197 |
| V |      |     |      |      |     |     |     |     |     |     |       |   |    |    |    |   |   |    |    |    |    |     |    |     |     |
| S |      |     |      |      |     |     |     |     |     |     |       |   |    |    |    |   |   |    |    |    |    |     |    |     |     |
| D | 4.2  | 1.1 | 5.4  | 0.00 | 0.1 | 0.0 | 0.0 | 0.4 | 0.1 | 0.1 | -     | 2 | 54 | 16 | 3  | 1 | 1 | 4  | 4  | 13 | 12 | 35  | 7  | 9   | 204 |

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| Sam<br>ple               | Analys<br>is |                  | Si<br>O <sub>2</sub><br>(%<br>) | Al <sub>2</sub><br>O <sub>3</sub><br>(%) | Fe <sub>2</sub><br>O <sub>3</sub><br>(%) | Mn<br>O<br>(%) | Mg<br>O<br>(%) | Ca<br>O<br>(%<br>) | Na <sub>2</sub><br>O<br>(%) | K <sub>2</sub><br>O<br>(%<br>) | Ti<br>O <sub>2</sub><br>(%<br>) | P <sub>2</sub><br>O <sub>5</sub><br>(%<br>) | Tot<br>al<br>(%) | As<br><br>PP<br>m | Ba<br><br>PP<br>m | Cr<br><br>PP<br>m | Cu<br><br>PP<br>m | Ga<br><br>PP<br>m | Nb<br><br>PP<br>m | Ni<br><br>PP<br>m | Pb<br><br>PP<br>m | Rb<br><br>PP<br>m | Sr<br><br>PP<br>m | V<br><br>PP<br>m | Y<br><br>PP<br>m | Zn<br><br>PP<br>m | Zr<br><br>PP<br>m |
|--------------------------|--------------|------------------|---------------------------------|------------------------------------------|------------------------------------------|----------------|----------------|--------------------|-----------------------------|--------------------------------|---------------------------------|---------------------------------------------|------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|------------------|------------------|-------------------|-------------------|
| 1377<br>3<br>(shal<br>e) | Su<br>rf     | 1                | 47.2                            | 16.5                                     | 27.7                                     | 0.06           | 2.5            | 0.5                | 0.6                         | 3.4                            | 0.8                             | 0.7                                         | 100              | 23                | 279               | 174               | 14                | 17                | 15                | 17                | 54                | 135               | 82                | 149              | 10               | 24                | 163               |
|                          |              | 2                | 46.4                            | 19.3                                     | 25.9                                     | 0.05           | 2.5            | 0.4                | 0.5                         | 3.5                            | 0.8                             | 0.6                                         | 100              | 19                | 666               | 163               | 8                 | 19                | 17                | 23                | 85                | 125               | 130               | 184              | 23               | 29                | 153               |
|                          |              | 3                | 44.2                            | 17.1                                     | 29.2                                     | 0.08           | 2.5            | 0.7                | 0.8                         | 3.7                            | 0.9                             | 1.0                                         | 100              | 25                | 1043              | 176               | 12                | 22                | 19                | nd                | 95                | 144               | 137               | 210              | 14               | 32                | 196               |
|                          |              | A<br>V<br>S<br>D | 45.9                            | 17.7                                     | 27.6                                     | 0.06           | 2.5            | 0.5                | 0.7                         | 3.5                            | 0.8                             | 0.7                                         | 100.0            | 22                | 663               | 171               | 11                | 19                | 17                | 20                | 78                | 135               | 116               | 181              | 16               | 28                | 171               |
|                          |              |                  | 1.6                             | 1.5                                      | 1.6                                      | 0.01           | 0.1            | 0.1                | 0.1                         | 0.1                            | 0.1                             | 0.0                                         | 0.2              | -                 | 3                 | 382               | 7                 | 3                 | 3                 | 2                 | 4                 | 21                | 10                | 30               | 31               | 7                 | 4                 |
|                          | Se<br>ct     | 1                | 52.1                            | 15.4                                     | 26.4                                     | 0.06           | 0.7            | 0.1                | 0.1                         | 3.9                            | 0.9                             | 0.3                                         | 100              | 11                | 518               | 184               | 8                 | 17                | 16                | 24                | 88                | 168               | 107               | 130              | 48               | 106               | 260               |
|                          |              | 2                | 53.9                            | 15.9                                     | 23.7                                     | 0.05           | 0.9            | 0.2                | 0.1                         | 4.1                            | 0.9                             | 0.3                                         | 100              | 7                 | 348               | 107               | 3                 | 18                | 19                | 24                | 96                | 178               | 109               | 191              | 34               | 107               | 216               |
|                          |              | 3                | 54.2                            | 15.6                                     | 23.9                                     | 0.05           | 0.8            | 0.1                | 0.2                         | 4.1                            | 0.8                             | 0.2                                         | 100              | 8                 | 501               | 132               | 3                 | 16                | 17                | 20                | 89                | 164               | 112               | 195              | 30               | 108               | 214               |
|                          |              | 4                | 51.3                            | 14.4                                     | 28.6                                     | 0.07           | 0.8            | 0.2                | 0.2                         | 3.5                            | 0.8                             | 0.2                                         | 100              | 12                | 463               | 177               | 4                 | 17                | 14                | 18                | 64                | 154               | 59                | 191              | 16               | 88                | 183               |
|                          |              | A<br>V<br>S<br>D | 52.9                            | 15.3                                     | 25.7                                     | 0.06           | 0.8            | 0.1                | 0.2                         | 3.9                            | 0.8                             | 0.2                                         | 100.0            | 10                | 458               | 150               | 5                 | 17                | 17                | 22                | 84                | 166               | 97                | 177              | 32               | 102               | 218               |
|                          |              | 1.4              | 0.6                             | 2.3                                      | 0.01                                     | 0.1            | 0.0            | 0.0                | 0.3                         | 0.1                            | 0.0                             | -                                           | 2                | 77                | 37                | 2                 | 1                 | 2                 | 3                 | 14                | 10                | 25                | 31                | 13               | 10               | 32                |                   |
| 1374<br>1<br>(ferr)      | Su<br>rf     | 1                | 4.0                             | 1.6                                      | 87.4                                     | 0.17           | 1.7            | 0.4                | 1.3                         | 1.0                            | 0.0                             | 2.3                                         | 100              | 22                | nd                | nd                | 22                | 3                 | 2                 | 146               | 120               | 3                 | 18                | 141              | 19               | 1342              | 22                |
|                          |              | 2                | 6.5                             | 1.6                                      | 84.9                                     | 0.21           | 1.6            | 0.4                | 1.4                         | 1.0                            | 0.0                             | 2.3                                         | 100              | 28                | 150               | nd                | 18                | nd                | nd                | 161               | 106               | 4                 | 23                | 93               | 17               | 1328              | 21                |
|                          |              | 3                | 3.0                             | 1.3                                      | 88.3                                     | 0.20           | 1.7            | 0.5                | 1.6                         | 1.0                            | 0.0                             | 2.5                                         | 100              | 11                | nd                | nd                | 28                | 5                 | nd                | 186               | 142               | 2                 | 21                | 56               | 20               | 1426              | 25                |
|                          |              | A<br>V<br>S<br>D | 4.5                             | 1.5                                      | 86.9                                     | 0.20           | 1.7            | 0.4                | 1.4                         | 1.0                            | 0.0                             | 2.4                                         | 100.0            | 20                | 150               | nd                | 23                | 4                 | 2                 | 164               | 123               | 3                 | 21                | 97               | 19               | 1365              | 23                |
|                          |              |                  | 1.8                             | 0.2                                      | 1.8                                      | 0.02           | 0.1            | 0.0                | 0.1                         | 0.0                            | 0.0                             | 0.1                                         | -                | 9                 | nd                | nd                | 5                 | 1                 | nd                | 20                | 18                | 1                 | 3                 | 43               | 2                | 53                | 2                 |
|                          | Se<br>ct     | 1                | 2.8                             | 1.0                                      | 91.5                                     | 0.10           | 0.6            | 0.4                | 0.7                         | 0.4                            | 0.0                             | 2.4                                         | 100              | 16                | nd                | nd                | 13                | nd                | nd                | 171               | 135               | 2                 | 16                | 93               | 19               | 1988              | 19                |
|                          |              | 2                | 2.5                             | 0.9                                      | 91.9                                     | 0.10           | 0.6            | 0.4                | 0.8                         | 0.4                            | 0.0                             | 2.5                                         | 100              | 17                | nd                | nd                | 9                 | 2                 | nd                | 156               | 117               | 2                 | 16                | 71               | 19               | 1991              | 17                |
|                          |              | 3                | 3.1                             | 0.9                                      | 91.4                                     | 0.11           | 0.7            | 0.4                | 0.6                         | 0.5                            | 0.0                             | 2.3                                         | 100              | 10                | 58                | nd                | 17                | nd                | 2                 | 176               | 129               | 5                 | 12                | 74               | 19               | 1992              | 16                |
|                          |              | 4                | 19.4                            | 1.7                                      | 74.7                                     | 0.11           | 0.9            | 0.3                | 0.5                         | 0.4                            | 0.0                             | 2.0                                         | 100              | 20                | 78                | 28                | 14                | 2                 | nd                | 127               | 75                | 4                 | 10                | 114              | 18               | 1390              | 13                |
|                          |              | A<br>V<br>S<br>D | 6.9                             | 1.1                                      | 87.4                                     | 0.11           | 0.7            | 0.4                | 0.6                         | 0.4                            | 0.0                             | 2.3                                         | 100.0            | 16                | 68                | 28                | 13                | 2                 | 2                 | 158               | 114               | 3                 | 14                | 88               | 19               | 1840              | 16                |
|                          |              | 8.3              | 0.4                             | 8.4                                      | 0.00                                     | 0.1            | 0.1            | 0.1                | 0.0                         | 0.0                            | 0.2                             | -                                           | 4                | 14                | nd                | 3                 | 0                 | nd                | 22                | 27                | 2                 | 3                 | 20                | 1                | 300              | 3                 |                   |

*In italic: values close to the detection limit; nd: not detected.*