Supplementary tables:

Supplementary Table S1: Precision RSD [%] and recovery [%] of the analyzed elements in the CRMs Loess and Cast and the in-house standard FLW-3 QR, that was used to verify precision and accuracy during the measurement of trace elements on the ICP-OES

|  |  |  |  |
| --- | --- | --- | --- |
|  | **LOESS** | **CAST** | **FLW-3 QC** |
| **Element** | **Precision RSD [%]** | **Recovery [%]** | **Precision RSD [%]** | **Recovery [%]** | **Precision RSD [%]** | **Recovery [%]** |
| **Al** | 1.02 | 98.55 | 0.73 | 96.17 | 3.16 | 105.83 |
| **Fe** | 3.01 | 98.62 | 1.45 | 94.95 | 1.62 | 103.32 |
| **Mn** | 3.71 | 102.43 | 2.32 | 95.80 | 0.77 | 76.05 |
| **Ba** | 0.95 | 98.70 | 1.17 | 99.82 | 2.26 | 98.70 |
| **Mo** | / | 176.94 | / | 100.63 | 1.14 | 98.08 |
| **V** | 3.09 | 101.82 | 1.06 | 92.07 | 0.26 | 96.24 |
| **Zn** | 0.86 | 112.76 | 0.08 | 100.68 | 1.20 | 99.00 |

Supplementary Table S2: Precision RSD [%] and recovery [%] of the analyzed elements in the CRM HISS-I, that underwent the total digestion with the analyzed samples. HISS-I (1, 2) measured by ICP-OES

|  |  |  |
| --- | --- | --- |
| **Element** | **HISS-I (1)**  | **HISS-I (2)**  |
|  | **Precision RSD [%]** | **Recovery [%]** | **Precision RSD [%]** | **Recovery [%]** |
| **Al** | 0.48 | 96.55 | 0.72 | 49.04 |
| **Fe** | 1.93 | 97.12 | 2.84 | 94.40 |
| **Mn** | 2.58 | 92.76 | 2.22 | 94.97 |
| **Ba** | 1.02 | 105.11 | 1.86 | 95.92 |
| **Mo** | / | 326.01 | / | 406.15 |
| **V** | 13.06 | 76.16 | 7.50 | 80.43 |
| **Zn** | 7.16 | 74.41 | 6.25 | 79.16 |

Supplementary Table S3: Recovery [%] of the analyzed elements in the CRM HISS-I, that underwent total digestion with the analyzed samples measured on the ICP-MS

|  |  |  |
| --- | --- | --- |
| **Element** | **HISS-I (1)**  | **HISS-I (2)**  |
|  | **Recovery [%]** | **Recovery [%]** |
| **Al** | 47.24 | 59.33 |
| **Fe** | 64.66 | 65.39 |
| **Mn** | 96.61 | 96.61 |
| **Ba** | 107.52 | 99.13 |
| **Mo** | -455.15 | -670.08 |
| **V** | 46.54 | 71.92 |
| **Zn** | 0.04 | -14.15 |
| **U** | 129.81 | 112.88 |

Supplementary Table S4: Precision RSD [%], accuracy RSD [%] and recovery of the analyzed elements in the CRMs CAST and DR-BS and the in-house standards FLW 3 QR and FLW 4 QR that were used to verify precision and accuracy during the measurement of reactive metal phases on the ICP-OES

|  |  |  |  |
| --- | --- | --- | --- |
| **Element** | **CAST (1)** | **CAST (2)** | **CAST (3)** |
|  | Precision RSD [%] | Recovery [%] | Precision RSD [%] | Recovery [%] | Precision RSD [%] | Recovery [%] |
| **Fe** | 1.81 | 96.14 | 2.31 | 96.82 | 1.81 | 95.91 |
| **Mn** | 2.09 | 98.85 | 2.12 | 98.99 | 2.21 | 96.10 |
|  | **CAST (4)** | **DR-BS (1)** | **DR-BS (2)** |
|  | Precision RSD [%] | Recovery [%] | Precision RSD [%] | Recovery [%] | Precision RSD [%] | Recovery [%] |
| **Fe** | 2.11 | 91.05 | 2.86 | 97.61 | 2.18 | 93.91 |
| **Mn** | 2.39 | 93.29 | / | 109.25 | / | 105.65 |
|  | **FLW-3 QC (1)** | **FLW-3 QC (2)** | **FLW-3 QC (3)** |
|  | Precision RSD [%] | Recovery [%]] | Precision RSD [%] | Recovery [%] | Precision RSD [%] | Recovery [%] |
| **Fe** | 0.18 | 105.40 | 0.16 | 105.85 | 0.42 | 105.06 |
| **Mn** | 0.79 | 99.27 | 0.81 | 100.79 | 0.63 | 99.17 |
|  | **FLW-3 QC (4)** | **FLW-4 QC (1)** | **FLW-4 QC (2)** |
|  | Precision RSD [%] | Recovery [%] | Precision RSD [%] | Recovery [%] | Precision RSD [%] | Recovery [%] |
| **Fe** | 4.72 | 95.78 | 1.02 | 104.77 | 0.04 | 98.86 |
| **Mn** | 0.68 | 94.98 | 0.13 | 98.56 | 0.10 | 96.05 |

Supplementary Table S: Organic carbon concentrations received by the leaching process, the control experiment and from previous work (Watts, 2019)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **Depth [cmbsf]** | **Leach OC [%]** | **Control OC [%]** | **Watts OC [%]** |
| **K-17** | 17 | 0.42 | 0.37 | 0.20 |
| **K-18** | 18 | 0.37 | / | 0.20 |
| **K-20** | 20 | 0.32 | 0.36 | 0.17 |
| **K-21** | 21 | 0.33 | 0.31 | 0.16 |
| **K-23** | 23 | 0.30 | 0.27 | 0.19 |
| **K-24** | 24 | 0.36 | 0.29 | 0.16 |
| **K-25** | 25 | 0.32 | 0.38 | 0.16 |
| **K-26** | 26 | 0.36 | 0.56 | 0.14 |
| **K-27** | 27 | 0.36 | 0.51 | 0.14 |
| **K-28** | 28 | 0.28 | 0.37 | 0.15 |
| **K-29** | 29 | 0.52 | 0.64 | 0.15 |
| **K-30** | 30 | 0.33 | 0.38 | 0.19 |
| **K-75** | 75 | 0.58 | 0.60 | / |
| **J-94** | 169 | 0.54 | 0.49 | 0.23 |
| **J-97** | 172 | 0.66 | / | 0.16 |
| **J-99** | 174 | 0.22 | / | 0.05 |
| **J-101** | 176 | 0.29 | / | 0.12 |
| **J-102** | 177 | 0.27 | 0.28 | 0.21 |
| **J-103** | 178 | 0.34 | 0.36 | 0.31 |
| **J-104** | 179 | 0.37 | 0.36 | 0.21 |
| **J-105** | 180 | 0.39 | 0.33 | 0.28 |
| **J-106** | 181 | 0.39 | 0.31 | 0.31 |
| **J-107** | 182 | 0.39 | 0.39 | 0.36 |
| **J-108** | 183 | 0.48 | 0.39 | 0.37 |
| **J-109** | 184 | 0.42 | 0.32 | 0.26 |
| **J-110** | 185 | 0.44 | 0.47 | 0.24 |
| **J-120** | 195 | 0.39 | 0.41 | 0.18 |
| **I-1** | 200 | 0.39 | 0.43 | 0.20 |
| **I-11** | 210 | 0.41 | 0.36 | 0.19 |
| **I-21** | 220 | 0.47 | 0.48 | 0.18 |

Supplementary Table S: Concentrations of trace metals and main elements

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Depth [cmbsf]** | **Mo [ppm]** | **U [ppm]** | **V [ppm]** | **Mn [ppm]** | **Zn [ppm]** | **Ba [ppm]** | **Fe [%]** | **Al [%]** |
| **K-20** | 20 | 1.46 | / | 91.48 | 574.73 | 90.80 | 399.25 | 3.26 | 5.32 |
| **K-21** | 21 | 1.77 | / | 93.26 | 572.60 | 95.83 | 400.32 | 3.15 | 5.70 |
| **K-23** | 23 | 1.53 | / | 88.01 | 541.76 | 97.17 | 411.60 | 3.16 | 5.76 |
| **K-24** | 24 | 1.53 | / | 96.83 | 554.02 | 95.61 | 423.21 | 3.36 | 5.48 |
| **K-25** | 25 | 1.85 | / | 98.18 | 561.48 | 93.16 | 431.73 | 3.38 | 5.80 |
| **K-26** | 26 | 1.22 | / | 86.91 | 546.34 | 87.71 | 420.87 | 3.15 | 6.37 |
| **K-28** | 28 | 1.49 | / | 85.42 | 573.16 | 73.42 | 432.60 | 3.23 | 5.89 |
| **K-29** | 29 | 0.52 | 2.43 | 69.05 | 706.72 | 73.29 | 446.10 | 3.16 | 5.74 |
| **K-30** | 30 | 0.78 | 2.45 | 70.90 | 818.97 | 88.97 | 454.10 | 3.31 | 5.85 |
| **K-75** | 75 | 9.09 | 2.85 | 58.37 | 579.48 | 74.64 | 468.43 | 3.07 | 5.84 |
| **J-94** | 169 | 0.05 | 1.46 | 76.65 | 781.56 | 53.07 | 201.24 | 2.39 | 2.77 |
| **J-95** | 170 | 0.00 | 1.50 | 70.89 | 926.40 | 27.90 | 194.64 | 2.74 | 2.98 |
| **J-96** | 171 | 0.00 | 1.44 | 109.55 | 888.22 | 37.16 | 197.55 | 3.40 | 3.53 |
| **J-97** | 172 | 1.37 | 1.43 | 87.91 | 906.27 | 71.61 | 175.64 | 3.24 | 3.37 |
| **J-99** | 174 | 0.05 | 1.18 | 205.60 | 1087.64 | 81.35 | 155.01 | 6.35 | 5.23 |
| **J-100** | 175 | 0.40 | 0.64 | 246.26 | 1326.13 | 105.96 | 112.80 | 8.35 | 6.29 |
| **J-101** | 176 | 1.24 | 1.32 | 60.65 | 438.94 | 41.92 | 244.74 | 2.83 | 4.05 |
| **J-102** | 177 | 0.00 | 1.53 | 53.63 | 416.99 | 37.76 | 289.90 | 2.07 | 3.66 |
| **J-103** | 178 | 0.95 | 1.80 | 50.98 | 377.21 | 43.80 | 319.60 | 2.22 | 3.94 |
| **J-104** | 179 | 0.74 | 2.19 | 65.87 | 470.53 | 59.50 | 341.90 | 3.04 | 5.70 |
| **J-105** | 180 | 0.79 | 2.29 | 66.18 | 402.16 | 56.08 | 367.95 | 3.08 | 5.49 |
| **J-106** | 181 | 1.37 | / | 79.88 | 285.20 | 57.50 | 375.83 | 2.76 | 5.32 |
| **J-107** | 182 | 1.37 | / | 97.06 | 314.24 | 68.13 | 405.05 | 3.04 | 5.70 |
| **J-108** | 183 | 3.20 | / | 101.69 | 321.92 | 66.81 | 375.01 | 2.92 | 5.76 |
| **J-109** | 184 | 1.97 | / | 91.73 | 338.75 | 64.13 | 356.58 | 2.90 | 5.48 |
| **J-120** | 195 | 1.61 | / | 99.53 | 399.49 | 65.72 | 350.20 | 3.47 | 5.80 |
| **I-11** | 210 | 1.59 | / | 95.91 | 566.93 | 74.14 | 367.89 | 3.56 | 6.37 |

Supplementary Table S: Enrichment factors of molybdenum. uranium. vanadium. manganese. nickel. copper. zinc. iron and the concentration of biogenic barium [ppm]. with PAAS as detrital source

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Depth [cmbsf]** | **Mo** | **U** | **V** | **Mn** | **Zn** | **Fe** | **BaBio** |
| **K-20** | 20 | 1.87 | / | 1.17 | 1.08 | 1.59 | 1.12 | 48.44 |
| **K-21** | 21 | 2.11 | / | 1.11 | 1.00 | 1.56 | 1.00 | 24.21 |
| **K-23** | 23 | 1.81 | / | 1.04 | 0.94 | 1.57 | 1.00 | 31.22 |
| **K-24** | 24 | 1.90 | / | 1.20 | 1.01 | 1.62 | 1.11 | 61.25 |
| **K-25** | 25 | 2.17 | / | 1.15 | 0.97 | 1.49 | 1.06 | 49.14 |
| **K-26** | 26 | 1.30 | / | 0.93 | 0.86 | 1.28 | 0.90 | 0.17 |
| **K-28** | 28 | 1.72 | / | 0.99 | 0.97 | 1.16 | 1.00 | 44.16 |
| **K-29** | 29 | 0.62 | 0.98 | 0.82 | 1.23 | 1.19 | 1.00 | 67.49 |
| **K-30** | 30 | 0.91 | 1.02 | 0.82 | 1.40 | 1.42 | 1.03 | 68.15 |
| **K-75** | 75 | 10.59 | 1.16 | 0.68 | 0.99 | 1.19 | 0.95 | 83.18 |
| **J-94** | 169 | 0.13 | 0.59 | 1.88 | 2.82 | 1.78 | 1.57 | 18.61 |
| **J-95** | 170 | 0.00 | 1.29 | 1.62 | 3.11 | 0.87 | 1.67 | -2.25 |
| **J-96** | 171 | 0.00 | 1.15 | 2.11 | 2.52 | 0.98 | 1.75 | -35.16 |
| **J-97** | 172 | 2.77 | 0.97 | 1.78 | 2.69 | 1.98 | 1.75 | -46.46 |
| **J-99** | 174 | 0.07 | 0.84 | 2.67 | 2.08 | 1.45 | 2.21 | -190.03 |
| **J-100** | 175 | 0.43 | 0.29 | 2.66 | 2.11 | 1.57 | 2.41 | -302.47 |
| **J-101** | 176 | 2.09 | 0.50 | 1.02 | 1.08 | 0.96 | 1.27 | -22.50 |
| **J-102** | 177 | 0.00 | 0.90 | 1.00 | 1.14 | 0.96 | 1.03 | 48.28 |
| **J-103** | 178 | 1.63 | 1.17 | 0.88 | 0.96 | 1.03 | 1.02 | 59.40 |
| **J-104** | 179 | 0.88 | 1.32 | 0.79 | 0.83 | 0.97 | 0.97 | -34.38 |
| **J-105** | 180 | 0.98 | 0.95 | 0.82 | 0.73 | 0.95 | 1.02 | 5.76 |
| **J-106** | 181 | 1.75 | / | 1.02 | 0.54 | 1.01 | 0.95 | 25.02 |
| **J-107** | 182 | 1.64 | / | 1.16 | 0.55 | 1.11 | 0.97 | 28.94 |
| **J-108** | 183 | 3.77 | / | 1.20 | 0.56 | 1.08 | 0.92 | -5.37 |
| **J-109** | 184 | 2.44 | / | 1.14 | 0.62 | 1.09 | 0.96 | -5.38 |
| **J-120** | 195 | 1.89 | / | 1.17 | 0.69 | 1.05 | 1.09 | -32.39 |
| **I-11** | 210 | 1.70 | / | 1.02 | 0.89 | 1.08 | 1.02 | -52.82 |

Supplementary Table S: Concentrations of reactive iron phases and reactive manganese phases

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Depth [cmbsf]** | **FeR [%]** | **MnR [%]** |
| **K-17** | 17 | 0.52 | 0.033 |
| **K-18** | 18 | 0.27 | 0.013 |
| **K-20** | 20 | 0.65 | 0.040 |
| **K-21** | 21 | 0.57 | 0.035 |
| **K-23** | 23 | 0.57 | 0.032 |
| **K-24** | 24 | 0.61 | 0.033 |
| **K-25** | 25 | 0.62 | 0.034 |
| **K-26** | 26 | 0.58 | 0.033 |
| **K-27** | 27 | 0.66 | 0.042 |
| **K-28** | 28 | 0.69 | 0.036 |
| **K-29** | 29 | 0.62 | 0.034 |
| **K-30** | 30 | 0.65 | 0.040 |
| **K-75** | 75 | 0.32 | 0.016 |
| **J-94** | 169 | 0.20 | 0.033 |
| **J-97** | 172 | 0.22 | 0.032 |
| **J-99** | 174 | 0.15 | 0.006 |
| **J-101** | 176 | 0.11 | 0.005 |
| **J-102** | 177 | 0.20 | 0.008 |
| **J-103** | 178 | 0.27 | 0.008 |
| **J-104** | 179 | 0.43 | 0.015 |
| **J-105** | 180 | 0.48 | 0.012 |
| **J-106** | 181 | 0.37 | 0.007 |
| **J-107** | 182 | 0.42 | 0.009 |
| **J-108** | 183 | 0.42 | 0.014 |
| **J-109** | 184 | 0.40 | 0.014 |
| **J-110** | 185 | 0.54 | 0.015 |
| **J-120** | 195 | 0.85 | 0.020 |
| **I-1** | 200 | 0.79 | 0.003 |
| **I-11** | 210 | 0.70 | 0.037 |
| **I-21** | 220 | 0.71 | 0.039 |

Supplementary Table S9: Values of reference materials BHVO-2 (Jochum et al., 2016). JB‑3 (Govindaraju, 1994). JA-2 (Jochum et al., 2016) and PAAS (McLennan et al., 1983) for elements used in the analysis

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | BHVO-2 | JB-3 | JA-2 | PAAS |
| Element | value | unit | value | unit | value | unit | value | unit |
| Al2O3 | 13.44 | % | 17.2 | % | 15.51 | % | 16.7 | % |
| Fe2O3 | 12.39 | % | 14.25 | % | 6.289 | % | 6.9 | % |
| MnO | 0.169 | % | 0.177 | % | 0.1092 | % | 0.11 | % |
| Mo | 4.07 | ppm | 1.09 | ppm | 0.581 | ppm | 1.3 | ppm |
| U | 0.412 | ppm | 0.48 | ppm | 2.182 | ppm | 3.7 | ppm |
| V | 318.2 | ppm | 372 | ppm | 119.7 | ppm | 130 | ppm |
| Zn | 103.9 | ppm | 38 | ppm | 64.5 | ppm | 95 | ppm |
| Ba | 130.9 | ppm | 245 | ppm | 308.4 | ppm | 580 | ppm |

Supplementary Table S10: Enrichment factors of Mo. U and V calculated with the reference materials BHVO-2. JB-3. JA-2 and PAAS

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|   | PAAS | JA-2 | JB-3 | BHVO-2 | PAAS | JA-2 | JB-3 | BHVO-2 | PAAS | JA-2 | JB-3 | BHVO-2 |
| Depth [cmbsf] | Mo | Mo | Mo | Mo | U | U | U | U | V | V | V | V |
| 20 | 1.87 | 3.88 | 2.30 | 0.48 |   |   |   |   | 1.17 | 1.18 | 0.42 | 0.38 |
| 21 | 2.11 | 4.38 | 2.59 | 0.54 |   |   |   |   | 1.11 | 1.12 | 0.40 | 0.37 |
| 23 | 1.81 | 3.76 | 2.22 | 0.47 |   |   |   |   | 1.04 | 1.05 | 0.37 | 0.34 |
| 24 | 1.90 | 3.94 | 2.33 | 0.49 |   |   |   |   | 1.20 | 1.21 | 0.43 | 0.39 |
| 25 | 2.17 | 4.50 | 2.67 | 0.56 |   |   |   |   | 1.15 | 1.16 | 0.41 | 0.38 |
| 26 | 1.30 | 2.70 | 1.60 | 0.33 |   |   |   |   | 0.93 | 0.94 | 0.33 | 0.30 |
| 28 | 1.72 | 3.57 | 2.11 | 0.44 |   |   |   |   | 0.99 | 1.00 | 0.36 | 0.32 |
| 29 | 0.62 | 1.29 | 0.76 | 0.16 | 0.98 | 1.60 | 8.04 | 7.32 | 0.82 | 0.83 | 0.29 | 0.27 |
| 30 | 0.91 | 1.89 | 1.12 | 0.23 | 1.02 | 1.58 | 7.96 | 7.25 | 0.82 | 0.83 | 0.30 | 0.27 |
| 75 | 10.59 | 21.97 | 13.01 | 2.72 | 1.16 | 1.84 | 9.27 | 8.44 | 0.68 | 0.69 | 0.24 | 0.22 |
| 169 | 0.13 | 0.27 | 0.16 | 0.03 | 0.59 | 1.98 | 9.99 | 9.09 | 1.88 | 1.90 | 0.68 | 0.62 |
| 170 | 0.00 | 0.00 | 0.00 | 0.00 | 1.29 | 1.89 | 9.55 | 8.69 | 1.62 | 1.63 | 0.58 | 0.53 |
| 171 | 0.00 | 0.00 | 0.00 | 0.00 | 1.15 | 1.53 | 7.73 | 7.04 | 2.11 | 2.13 | 0.76 | 0.69 |
| 172 | 2.77 | 5.75 | 3.40 | 0.71 | 0.97 | 1.60 | 8.08 | 7.36 | 1.78 | 1.79 | 0.64 | 0.58 |
| 174 | 0.07 | 0.15 | 0.09 | 0.02 | 0.84 | 0.85 | 4.29 | 3.91 | 2.67 | 2.70 | 0.96 | 0.88 |
| 175 | 0.43 | 0.89 | 0.53 | 0.11 | 0.29 | 0.38 | 1.94 | 1.76 | 2.66 | 2.68 | 0.96 | 0.88 |
| 176 | 2.09 | 4.34 | 2.57 | 0.54 | 0.50 | 1.23 | 6.19 | 5.64 | 1.02 | 1.03 | 0.37 | 0.33 |
| 177 | 0.00 | 0.00 | 0.00 | 0.00 | 0.90 | 1.57 | 7.92 | 7.21 | 1.00 | 1.00 | 0.36 | 0.33 |
| 178 | 1.63 | 3.38 | 2.00 | 0.42 | 1.17 | 1.72 | 8.67 | 7.90 | 0.88 | 0.89 | 0.32 | 0.29 |
| 179 | 0.88 | 1.83 | 1.08 | 0.23 | 1.32 | 1.44 | 7.28 | 6.63 | 0.79 | 0.79 | 0.28 | 0.26 |
| 180 | 0.98 | 2.03 | 1.20 | 0.25 | 0.95 | 1.57 | 7.90 | 7.19 | 0.82 | 0.83 | 0.30 | 0.27 |
| 181 | 1.75 | 3.63 | 2.15 | 0.45 |   |   |   |   | 1.02 | 1.03 | 0.37 | 0.34 |
| 182 | 1.64 | 3.40 | 2.01 | 0.42 |   |   |   |   | 1.16 | 1.17 | 0.42 | 0.38 |
| 183 | 3.77 | 7.82 | 4.63 | 0.97 |   |   |   |   | 1.20 | 1.21 | 0.43 | 0.39 |
| 184 | 2.44 | 5.06 | 3.00 | 0.63 |   |   |   |   | 1.14 | 1.15 | 0.41 | 0.37 |
| 195 | 1.89 | 3.92 | 2.32 | 0.49 |   |   |   |   | 1.17 | 1.18 | 0.42 | 0.38 |
| 210 | 1.70 | 3.53 | 2.09 | 0.44 |   |   |   |   | 1.02 | 1.03 | 0.37 | 0.34 |

Supplementary Table S11: Enrichment factors of Mn and Fe calculated with the reference materials BHVO-2. JB-3. JA-2 and PAAS

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|   | PAAS | JA-2 | JB-3 | BHVO-2 | PAAS | JA-2 | JB-3 | BHVO-2 |
| Depth [cmbsf] | Mn | Mn | Mn | Mn | Fe | Fe | Fe | Fe |
| 20 | 1.08 | 1.05 | 0.72 | 0.59 | 1.12 | 1.15 | 0.56 | 0.50 |
| 21 | 1.00 | 0.98 | 0.67 | 0.55 | 1.00 | 1.03 | 0.50 | 0.45 |
| 23 | 0.94 | 0.91 | 0.62 | 0.51 | 1.00 | 1.02 | 0.50 | 0.45 |
| 24 | 1.01 | 0.98 | 0.67 | 0.55 | 1.11 | 1.14 | 0.56 | 0.50 |
| 25 | 0.97 | 0.94 | 0.64 | 0.53 | 1.06 | 1.09 | 0.53 | 0.48 |
| 26 | 0.86 | 0.83 | 0.57 | 0.47 | 0.90 | 0.92 | 0.45 | 0.41 |
| 28 | 0.97 | 0.95 | 0.65 | 0.53 | 1.00 | 1.03 | 0.50 | 0.45 |
| 29 | 1.23 | 1.20 | 0.82 | 0.67 | 1.00 | 1.03 | 0.50 | 0.45 |
| 30 | 1.40 | 1.36 | 0.93 | 0.76 | 1.03 | 1.06 | 0.52 | 0.46 |
| 75 | 0.99 | 0.96 | 0.66 | 0.54 | 0.95 | 0.98 | 0.48 | 0.43 |
| 169 | 2.82 | 2.74 | 1.88 | 1.54 | 1.57 | 1.61 | 0.79 | 0.71 |
| 170 | 3.11 | 3.01 | 2.06 | 1.69 | 1.67 | 1.71 | 0.84 | 0.75 |
| 171 | 2.52 | 2.45 | 1.67 | 1.37 | 1.75 | 1.80 | 0.88 | 0.79 |
| 172 | 2.69 | 2.61 | 1.79 | 1.46 | 1.75 | 1.80 | 0.88 | 0.79 |
| 174 | 2.08 | 2.02 | 1.38 | 1.13 | 2.21 | 2.27 | 1.11 | 1.00 |
| 175 | 2.11 | 2.05 | 1.40 | 1.15 | 2.41 | 2.48 | 1.21 | 1.09 |
| 176 | 1.08 | 1.05 | 0.72 | 0.59 | 1.27 | 1.30 | 0.64 | 0.57 |
| 177 | 1.14 | 1.11 | 0.76 | 0.62 | 1.03 | 1.06 | 0.52 | 0.46 |
| 178 | 0.96 | 0.93 | 0.64 | 0.52 | 1.02 | 1.05 | 0.51 | 0.46 |
| 179 | 0.83 | 0.80 | 0.55 | 0.45 | 0.97 | 1.00 | 0.49 | 0.44 |
| 180 | 0.73 | 0.71 | 0.49 | 0.40 | 1.02 | 1.05 | 0.51 | 0.46 |
| 181 | 0.54 | 0.52 | 0.36 | 0.29 | 0.95 | 0.97 | 0.47 | 0.43 |
| 182 | 0.55 | 0.54 | 0.37 | 0.30 | 0.97 | 0.99 | 0.49 | 0.44 |
| 183 | 0.56 | 0.54 | 0.37 | 0.30 | 0.92 | 0.95 | 0.46 | 0.42 |
| 184 | 0.62 | 0.60 | 0.41 | 0.34 | 0.96 | 0.99 | 0.48 | 0.43 |
| 195 | 0.69 | 0.67 | 0.46 | 0.37 | 1.09 | 1.12 | 0.55 | 0.49 |
| 210 | 0.89 | 0.86 | 0.59 | 0.48 | 1.02 | 1.04 | 0.51 | 0.46 |

Supplementary Table S12: Enrichment factor of Zn and BaBio concentrations [ppm] calculated with the reference materials BHVO-2. JB-3. JA-2 and PAAS

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | PAAS | JA-2 | JB-3 | BHVO-2 | PAAS | JA-2 | JB-3 | BHVO-2 |
| Depth [cmbsf] | Zn | Zn | Zn | Zn | BaBio [ppm] | BaBio [ppm] | BaBio [ppm] | BaBio [ppm] |
| 20 | 1.59 | 2.17 | 4.09 | 1.17 | 48.44 | 199.60 | 256.23 | 301.46 |
| 21 | 1.56 | 2.14 | 4.03 | 1.15 | 24.21 | 186.28 | 246.99 | 295.48 |
| 23 | 1.57 | 2.15 | 4.04 | 1.15 | 31.22 | 195.13 | 256.52 | 305.56 |
| 24 | 1.62 | 2.22 | 4.18 | 1.19 | 61.25 | 217.21 | 275.64 | 322.31 |
| 25 | 1.49 | 2.05 | 3.85 | 1.10 | 49.14 | 214.00 | 275.76 | 325.08 |
| 26 | 1.28 | 1.75 | 3.30 | 0.94 | 0.17 | 181.45 | 249.36 | 303.60 |
| 28 | 1.16 | 1.59 | 2.99 | 0.85 | 44.16 | 211.54 | 274.24 | 324.32 |
| 29 | 1.19 | 1.63 | 3.06 | 0.87 | 67.49 | 230.63 | 291.74 | 340.56 |
| 30 | 1.42 | 1.94 | 3.65 | 1.04 | 68.15 | 234.45 | 296.75 | 346.51 |
| 75 | 1.19 | 1.63 | 3.06 | 0.88 | 83.18 | 249.18 | 311.37 | 361.04 |
| 169 | 1.78 | 2.44 | 4.60 | 1.31 | 18.61 | 97.30 | 126.78 | 150.33 |
| 170 | 0.87 | 1.19 | 2.24 | 0.64 | -2.25 | 82.59 | 114.37 | 139.75 |
| 171 | 0.98 | 1.34 | 2.53 | 0.72 | -35.16 | 65.11 | 102.68 | 132.68 |
| 172 | 1.98 | 2.71 | 5.10 | 1.46 | -46.46 | 49.25 | 85.10 | 113.73 |
| 174 | 1.45 | 1.98 | 3.73 | 1.07 | -190.03 | -41.35 | 14.34 | 58.83 |
| 175 | 1.57 | 2.14 | 4.04 | 1.15 | -302.47 | -123.53 | -56.50 | -2.96 |
| 176 | 0.96 | 1.32 | 2.48 | 0.71 | -22.50 | 92.65 | 135.79 | 170.25 |
| 177 | 0.96 | 1.31 | 2.47 | 0.71 | 48.28 | 152.39 | 191.39 | 222.54 |
| 178 | 1.03 | 1.41 | 2.66 | 0.76 | 59.40 | 171.52 | 213.52 | 247.06 |
| 179 | 0.97 | 1.33 | 2.50 | 0.71 | -34.38 | 127.76 | 188.50 | 237.01 |
| 180 | 0.95 | 1.30 | 2.45 | 0.70 | 5.76 | 161.83 | 220.29 | 266.99 |
| 181 | 1.01 | 1.38 | 2.59 | 0.74 | 25.02 | 176.19 | 232.81 | 278.04 |
| 182 | 1.11 | 1.52 | 2.86 | 0.82 | 28.94 | 191.00 | 251.71 | 300.20 |
| 183 | 1.08 | 1.48 | 2.78 | 0.79 | -5.37 | 158.54 | 219.94 | 268.98 |
| 184 | 1.09 | 1.49 | 2.80 | 0.80 | -5.38 | 150.59 | 209.01 | 255.68 |
| 195 | 1.05 | 1.44 | 2.72 | 0.78 | -32.39 | 132.46 | 194.22 | 243.55 |
| 210 | 1.08 | 1.48 | 2.79 | 0.80 | -52.82 | 128.46 | 196.37 | 250.61 |