

Supplementary Material 1

Averages, standard deviation, accuracy, and method precision calculated from averages of each digested sample.

Table S1: Replicate analyses of MESS-3 reference material during ICP-OES measurements (n=13 digested samples, 10 ICP-OES runs).

| LOQ <sup>#</sup><br>[mg/kg] | Element   | MESS-3<br>reference<br>[mg/kg] | MESS-3<br>measured<br>[mg/kg] | Accuracy<br>(%) | Method<br>precision<br>(%RSD) |
|-----------------------------|-----------|--------------------------------|-------------------------------|-----------------|-------------------------------|
| 19-231                      | <b>Al</b> | 85900±2300                     | 68879±13622                   | -20             | 20                            |
| 13-158                      | <b>Ca</b> | 14700±600                      | 13291±1094                    | -10             | 8                             |
| 5-24                        | <b>Cu</b> | 33.9±1.6                       | 33±1                          | -3              | 4                             |
| 98-379                      | <b>Fe</b> | 43400±1100                     | 39219±2264                    | -10             | 6                             |
| 9-101                       | <b>Mn</b> | 324±12                         | 302±22                        | -7              | 7                             |
| 86-741                      | <b>P</b>  | 1200 <sup>a</sup>              | 1257±128                      | +5              | 10                            |
| 2-16                        | <b>Sr</b> | 129±11                         | 114±17                        | -11             | 15                            |
| 8-28                        | <b>V</b>  | 243±10                         | 233±17                        | -4              | 7                             |
| 4-15                        | <b>Zn</b> | 159±8                          | 147±6                         | -7              | 4                             |

<sup>#</sup> LOQ: limit of quantification; 10\*standard deviation of acid blanks for each run

<sup>a</sup> information value

Table S2: Replicate analyses of BHVO-2 reference material during ICP-OES measurements (n=13 digested samples, 10 ICP-OES runs).

| LOQ <sup>#</sup><br>[mg/kg] | Element   | BHVO-2<br>reference<br>[mg/kg] | BHVO-2<br>measured<br>[mg/kg] | Accuracy (%) | Method<br>precision<br>(%RSD) |
|-----------------------------|-----------|--------------------------------|-------------------------------|--------------|-------------------------------|
| 19-231                      | <b>Al</b> | 71600±800                      | 74535±1889                    | +4           | 3                             |
| 13-158                      | <b>Ca</b> | 81700±1200                     | 83017±2188                    | +2           | 3                             |
| 5-24                        | <b>Cu</b> | 127±7                          | 135±5                         | +7           | 3                             |
| 98-379                      | <b>Fe</b> | 86300±1400                     | 87880±2323                    | +2           | 3                             |
| 9-101                       | <b>Mn</b> | 1290±40                        | 1347±35                       | +4           | 3                             |
| 86-741                      | <b>P</b>  | 1200±100                       | 1307±143                      | +9           | 11                            |
| 2-16                        | <b>Sr</b> | 389±23                         | 392±10                        | +1           | 3                             |
| 8-28                        | <b>V</b>  | 317±11                         | 315±16                        | +22          | 19                            |
| 4-15                        | <b>Zn</b> | 103±6                          | 117±5                         | +14          | 5                             |

<sup>#</sup> LOQ: limit of quantification; 10\*standard deviation of acid blanks for each run

Table S3: Replicate analyses of MESS-3 reference material during ICP-MS measurements (n=13 digested samples, 8 ICP-MS runs; one less for Mo).

| Average LOQ <sup>#</sup> [mg/kg] | Element   | MESS-3 reference [mg/kg] | MESS-3 measured [mg/kg] | Accuracy (%) | Method precision (%RSD) |
|----------------------------------|-----------|--------------------------|-------------------------|--------------|-------------------------|
| 0.25                             | <b>Co</b> | 14.4±2                   | 14.5±0.5                | +1           | 4                       |
| 0.25                             | <b>Ni</b> | 46.9±2.2                 | 49.1±2                  | +5           | 4                       |
| 0.67                             | <b>Mo</b> | 2.78±0.07                | 2.78±0.16               | 0            | 6                       |
| 0.07                             | <b>U</b>  | 4b                       | 3.3±0.7                 | -17          | 21                      |

<sup>#</sup> LOQ: limit of quantification; 10\*standard deviation of acid blanks for each run

<sup>b</sup> information value

Table S4: Replicate analyses of BHVO-2 CRM during ICP-MS measurements (n=13 digested samples; 9 ICP-MS runs; one less for Co, Ni, Ba, Eu, and Tb).

| Average LOQ <sup>#</sup> [mg/kg] | Element | BHVO-2 recommended [mg/kg] | BHVO-2 measured [mg/kg] | Accuracy (%) | Precision (%) |
|----------------------------------|---------|----------------------------|-------------------------|--------------|---------------|
| 0.25                             | Co      | 45±3                       | 46±1                    | +2           | 3             |
| 0.25                             | Ni      | 119±7                      | 125±4                   | +5           | 3             |
| 0.58                             | Ba      | 130±13                     | 129±6                   | -1           | 5             |
| 0.10                             | Y       | 26±2                       | 25±1                    | -5           | 3             |
| 0.05                             | La      | 15±1                       | 16±1                    | +4           | 5             |
| 0.05                             | Ce      | 38±2                       | 39±2                    | +3           | 5             |
| 0.04                             | Pr      | ---                        | 5.5±0.3                 | ---          | 5             |
| 0.28                             | Nd      | 25.0±1.8                   | 25±1                    | 0            | 5             |
| 0.24                             | Sm      | 6.2±0.4b                   | 6.3±0.3                 | +1           | 5             |
| 0.09                             | Eu      | ---                        | 2.1±0.1                 | ---          | 5             |
| 0.15                             | Gd      | 6.3±0.2b                   | 6.7±0.4                 | +7           | 6             |
| 0.05                             | Tb      | 0.9b                       | 0.96±0.04               | +7           | 5             |
| 0.15                             | Dy      | ---                        | 5.5±0.3                 | ---          | 5             |
| 0.05                             | Ho      | 1.04±0.04b                 | 1.00±0.04               | -4           | 4             |
| 0.13                             | Er      | ---                        | 2.6±0.1                 | ---          | 5             |
| 0.05                             | Tm      | ---                        | 0.34±0.02               | ---          | 5             |
| 0.15                             | Yb      | 2.0±0.2b                   | 2.0±0.1                 | +2           | 4             |
| 0.04                             | Lu      | 0.28±0.01b                 | 0.28±0.02               | -2           | 6             |

<sup>#</sup> LOQ: limit of quantification; 10\*standard deviation of acid blanks for each run

<sup>b</sup> information value

Table S5: Replicate analyses of NASS-6 seawater certified reference material during ICP-MS measurements.

| LOQ <sup>#</sup><br>[μg/kg] | Element         | n (number<br>of ICP-<br>MS runs) | NASS-6<br>reference<br>[μg/kg] | NASS-6<br>measured<br>[μg/kg] | Accuracy<br>(%) | Method<br>precision<br>(%RSD) |
|-----------------------------|-----------------|----------------------------------|--------------------------------|-------------------------------|-----------------|-------------------------------|
| 0.029-0.80                  | <b>Cd</b>       | 3                                | 0.0303±0.0019                  | 0.037±0.0012                  | +22             | 3.1                           |
| 0.02-0.17                   | <b>U</b>        | 5                                | 3 <sup>a</sup>                 | 2.73±0.1                      | -9              | 3.7                           |
| 0.44-2.90                   | <b>V (KED)</b>  | 4                                | 1.42±0.16                      | 1.45±0.08                     | +2              | 5.5                           |
| 0.56-2.20                   | <b>Mn (KED)</b> | ---                              | 0.516±0.047                    | ---                           |                 |                               |
| 0.07-0.26                   | <b>Co (KED)</b> | ---                              | 0.015 <sup>a</sup>             | ---                           |                 |                               |
| 0.12-3                      | <b>Cu (KED)</b> | ---                              | 0.242±0.025                    | ---                           |                 |                               |
| 0.88-4.8                    | <b>As (KED)</b> | 2                                | 1.40±0.12                      | 1.22±0.02                     | -13             | 1.5                           |
| 0.3-5.7                     | <b>Mo (KED)</b> | 5                                | 9.66±0.70                      | 9.87±0.27                     | +2              | 2.7                           |

<sup>#</sup> LOQ: limit of quantification; 10\*standard deviation of acid blanks for each run

<sup>a</sup> information value

Table S6: Replicate analyses of NASS-7 seawater certified reference material during ICP-MS measurements.

| LOQ <sup>#</sup><br>[μg/kg] | Element         | n (number<br>of ICP-<br>MS runs) | NASS-7<br>reference<br>[μg/kg] | NASS-7<br>measured<br>[μg/kg] | Accuracy<br>(%) | Method<br>precision<br>(%RSD) |
|-----------------------------|-----------------|----------------------------------|--------------------------------|-------------------------------|-----------------|-------------------------------|
| 0.029-0.80                  | <b>Cd</b>       | 2                                | 0.0157±0.0016                  | 0.021±0.003                   | +34             | 14                            |
| 0.02-0.17                   | <b>U</b>        | 7                                | 2.81±0.16                      | 2.65±0.23                     | -6              | 8.6                           |
| 0.44-2.90                   | <b>V (KED)</b>  | 5                                | 1.27±0.08 <sup>a</sup>         | 1.38±0.15                     | +9              | 11                            |
| 0.56-2.20                   | <b>Mn (KED)</b> | 1                                | 0.74±0.06                      | 0.73                          | -1              | ---                           |
| 0.07-0.26                   | <b>Co (KED)</b> | ---                              | 0.0143±0.0014                  | ---                           |                 |                               |
| 0.12-3                      | <b>Cu (KED)</b> | ---                              | 0.195±0.014                    | ---                           |                 |                               |
| 0.88-4.8                    | <b>As (KED)</b> | 4                                | 1.23±0.06 <sup>a</sup>         | 1.14±0.12                     | -7              | 11                            |
| 0.3-5.7                     | <b>Mo (KED)</b> | 7                                | 9.10±0.40                      | 8.99±0.43                     | -1              | 4.8                           |

<sup>#</sup> LOQ: limit of quantification; 10\*standard deviation of acid blanks for each run

<sup>a</sup> reference value

Table 7: Replicate analyses of SLEW-3 estuarine water reference material during ICP-MS measurements (n= 7 ICP-MS runs). Runs for which the values were far below the LOQ were excluded.

| LOQ <sup>#</sup><br>[µg/kg] | Element         | n<br>(number<br>of ICP-<br>MS runs) | SLEW-3<br>reference<br>[µg/kg] | SLEW-3<br>measured<br>[µg/kg] | Accuracy<br>(%) | Method<br>precision<br>(%RSD) |
|-----------------------------|-----------------|-------------------------------------|--------------------------------|-------------------------------|-----------------|-------------------------------|
| 0.029-0.80                  | <b>Cd</b>       | 5                                   | 0.047±0.004                    | 0.052±0.003                   | +10             | 6.4                           |
| 0.02-0.17                   | <b>U</b>        | 7                                   | 1.8 <sup>b</sup>               | 1.51±0.12                     | -16             | 8.2                           |
| 0.44-2.90                   | <b>V (KED)</b>  | 7                                   | 2.54±0.31                      | 2.75±0.29                     | +8              | 10.7                          |
| 0.56-2.20                   | <b>Mn (KED)</b> | 6                                   | 1.59±0.22                      | 1.29±0.22                     | -19             | 17.4                          |
| 0.07-0.26                   | <b>Co (KED)</b> | ---                                 | 0.040±0.010                    | ---                           |                 |                               |
| 0.12-3                      | <b>Cu (KED)</b> | 6                                   | 1.53±0.12                      | 1.51±0.45                     | -1              | 30                            |
| 0.88-4.8                    | <b>As (KED)</b> | 2                                   | 1.34±0.09                      | 1.27±0.03                     | -5              | 2.2                           |
| 0.3-5.7                     | <b>Mo (KED)</b> | 7                                   | 5.1 <sup>b</sup>               | 4.7±0.3                       | -8              | 6.7                           |

<sup>#</sup> LOQ: limit of quantification; 10\*standard deviation of acid blanks for each run

<sup>b</sup> information value