Supplementary Table 1 $\delta^{65}$Cu values of reference materials ERM$^{\text{®}}$-AE647 and Romil determined by SN-MC-IC-MS using each of SSC-1, SSC-3, SSC-4 and CUPD-1 as a calibration standard.

| Reference Materials | Calibration Standards | $\delta^{65/63}$Cu$_{\text{SRM976}}$ (‰) | $U$ (‰, $k = 2)^a$ | 2 s.d. (%)$^b$ | n | Sources               |
|---------------------|-----------------------|------------------------------------------|-----------------|----------------|---|----------------------|
| ERM$^{\text{®}}$-AE647 | SSC-1                 | 0.18                                     | 0.08            | 0.06           | 19 | This study           |
|                     | SSC-3                 | 0.17                                     | 0.09            | 0.07           | 12 |                      |
|                     | SSC-4                 | 0.19                                     | 0.08            | 0.07           | 19 |                      |
|                     | CUPD-1                | 0.18                                     | 0.07            | 0.05           | 19 |                      |
|                     |                       |                                          |                 |                | 0.21 | Moeller et al. (2012) |
|                     |                       |                                          |                 |                | 0.04 |                      |
|                     |                       |                                          |                 |                | 60  |                      |
| Romil Cu            | SSC-1                 | 0.19                                     | 0.07            | 0.06           | 16 | This study           |
|                     | SSC-3                 | 0.17                                     | 0.08            | 0.07           | 17 |                      |
|                     | SSC-4                 | 0.18                                     | 0.07            | 0.07           | 19 |                      |
|                     | CUPD-1                | 0.16                                     | 0.07            | 0.06           | 19 |                      |
|                     |                       |                                          |                 |                | 0.18 | Moeller et al. (2012) |
|                     |                       |                                          |                 |                | 0.06 |                      |
|                     |                       |                                          |                 |                | 19  |                      |

$^a$: Combined measurement uncertainty, coverage factor $k = 2$ produces an interval having a level of confidence of approximately 95 percent; $^b$: precision is given as 2 standard deviation of the repeated measurements.
Supplementary Table 2 δ\textsuperscript{65}Cu values of native copper sample NMC 12864 determined by LA-MC-IC-MS using each of SSC-1, SSC-3, SSC-4 and CUPD-1 as a calibration standard.

| Sample Name | Calibration Standards | δ\textsuperscript{65/63}Cu\textsubscript{SRM976} (‰) | U (‰, k = 2)\textsuperscript{a} | 2 s.d. (‰)\textsuperscript{b} | n  |
|-------------|-----------------------|------------------|-----------------|-----------------|---|
| NMC 12864   | SSC-1                 | 0.51              | 0.07            | 0.06            | 10|
|             | SSC-3                 | 0.54              | 0.12            | 0.10            | 20|
|             | SSC-4                 | 0.53              | 0.09            | 0.07            | 10|
|             | CUPD-1                | 0.59              | 0.09            | 0.08            | 10|

\textsuperscript{a}: Combined measurement uncertainty, coverage factor \(k = 2\) produces an interval having a level of confidence of approximately 95 percent; \textsuperscript{b}: precision is given as 2 standard deviation of the repeated measurements.