

Table S1 Effect of acid molarity mismatch on Ca isotopic measurements.

| Acid molarity | $\delta^{44/40}\text{Ca}$ (‰) | 2 SD | $\delta^{44/42}\text{Ca}$ (‰) | 2 SD | $\epsilon^{40}\text{Ca}$ | 2 SD |
|---------------|-------------------------------|------|-------------------------------|------|--------------------------|------|
| 1 %           | 0.17                          | 0.09 | -0.21                         | 0.08 | -5.92                    | 0.12 |
| 2 %           | 0.02                          | 0.04 | 0.03                          | 0.06 | 0.34                     | 0.07 |
| 3 %           | 0.19                          | 0.09 | 0.55                          | 0.08 | 9.46                     | 0.12 |
| 4 %           | 0.18                          | 0.08 | 1.00                          | 0.05 | 18.71                    | 0.09 |
| 5 %           | 0.19                          | 0.08 | 1.35                          | 0.11 | 25.73                    | 0.14 |

Table S2 Effect of Ca concentration mismatch on Ca isotopic measurements.

| $\text{Ca}_{\text{sample}}/\text{Ca}_{\text{standard}}$ | $\delta^{44/40}\text{Ca}$ (‰) | 2 SD | $\delta^{44/42}\text{Ca}$ (‰) | 2 SD | $\epsilon^{40}\text{Ca}$ | 2 SD |
|---|-------------------------------|------|-------------------------------|------|--------------------------|------|
| 0.50  | -0.86                         | 0.08 | -0.11                         | 0.06 | 6.23                     | 0.10 |
| 0.80  | -0.27                         | 0.05 | -0.04                         | 0.05 | 1.90                     | 0.07 |
| 0.90  | -0.18                         | 0.07 | -0.04                         | 0.04 | 1.01                     | 0.08 |
| 0.95  | -0.08                         | 0.11 | -0.03                         | 0.09 | 0.21                     | 0.14 |
| 0.96  | -0.09                         | 0.14 | -0.05                         | 0.07 | -0.19                    | 0.16 |
| 0.97  | 0.02                          | 0.13 | 0.00                          | 0.08 | -0.27                    | 0.15 |
| 0.98  | -0.07                         | 0.10 | -0.05                         | 0.05 | -0.40                    | 0.11 |
| 0.99  | 0.00                          | 0.11 | -0.01                         | 0.05 | -0.23                    | 0.13 |
| 1   | 0.05                          | 0.05 | 0.04                          | 0.05 | 0.31                     | 0.07 |
| 1.01  | 0.01                          | 0.08 | 0.01                          | 0.05 | 0.04                     | 0.09 |
| 1.02  | 0.05                          | 0.08 | 0.05                          | 0.04 | 0.54                     | 0.09 |
| 1.03  | 0.00                          | 0.10 | -0.01                         | 0.07 | -0.16                    | 0.12 |
| 1.04  | 0.06                          | 0.06 | 0.06                          | 0.05 | 0.67                     | 0.08 |
| 1.05  | 0.08                          | 0.09 | 0.02                          | 0.05 | -0.36                    | 0.11 |
| 1.10  | 0.18                          | 0.03 | 0.03                          | 0.04 | -1.20                    | 0.05 |
| 1.20  | 0.28                          | 0.10 | 0.04                          | 0.05 | -1.90                    | 0.11 |
| 1.50  | 0.86                          | 0.07 | 0.11                          | 0.04 | -6.24                    | 0.09 |

Table S3 Effect of Ca concentration on Ca isotopic measurements.

| Ca concentration (ng g <sup>-1</sup> ) | $\delta^{44/40}\text{Ca}$ (‰) | 2 SD | $\delta^{44/42}\text{Ca}$ (‰) | 2 SD | $\epsilon^{40}\text{Ca}$ | 2 SD |
|--|-------------------------------|------|-------------------------------|------|--------------------------|------|
| 10                                     | 0.02                          | 0.19 | 0.10                          | 0.21 | 1.86                     | 0.28 |
| 20                                     | 0.02                          | 0.20 | 0.06                          | 0.16 | 1.20                     | 0.26 |
| 30                                     | -0.04                         | 0.23 | -0.04                         | 0.18 | -0.43                    | 0.30 |
| 50                                     | -0.08                         | 0.04 | -0.06                         | 0.05 | -0.38                    | 0.07 |
| 100                                    | 0.00                          | 0.08 | 0.01                          | 0.04 | 0.23                     | 0.09 |
| 150                                    | 0.02                          | 0.07 | 0.01                          | 0.06 | 0.06                     | 0.09 |

Table S4 Effect of matrix elements on Ca isotopic measurements.

| Matrix elements added | Element/Ca (Concentration ratio) | $\delta^{44/40}\text{Ca}$ (‰) | 2 SD | $\delta^{44/42}\text{Ca}$ (‰) | 2 SD | $\epsilon^{40}\text{Ca}$ | 2 SD |
|-----------------------|----------------------------------|-------------------------------|------|-------------------------------|------|--------------------------|------|
| Al                    | 0.1 %                            | -0.01                         | 0.09 | 0.03                          | 0.06 | 0.70                     | 0.10 |
|                       | 1 %                              | 0.00                          | 0.09 | 0.06                          | 0.05 | 1.23                     | 0.10 |
|                       | 2 %                              | -0.26                         | 0.07 | -0.08                         | 0.05 | 0.81                     | 0.09 |
|                       | 5 %                              | -0.48                         | 0.07 | -0.15                         | 0.10 | 1.71                     | 0.12 |
|                       | 10 %                             | -0.80                         | 0.11 | -0.22                         | 0.11 | 3.45                     | 0.16 |
| Na                    | 0.1 %                            | -0.08                         | 0.06 | -0.03                         | 0.08 | 0.24                     | 0.10 |
|                       | 1 %                              | -0.09                         | 0.06 | -0.03                         | 0.05 | 0.36                     | 0.08 |
|                       | 5 %                              | 0.03                          | 0.11 | 0.03                          | 0.05 | 0.32                     | 0.12 |
|                       | 10 %                             | -0.06                         | 0.10 | -0.02                         | 0.08 | 0.15                     | 0.13 |
| K                     | 0.1 %                            | -0.01                         | 0.10 | 0.01                          | 0.07 | 0.28                     | 0.13 |
|                       | 1 %                              | 0.00                          | 0.08 | 0.01                          | 0.06 | 0.15                     | 0.10 |
|                       | 2 %                              | -0.03                         | 0.10 | 0.02                          | 0.06 | 0.74                     | 0.12 |
|                       | 5 %                              | -0.10                         | 0.12 | -0.07                         | 0.08 | -0.36                    | 0.14 |
|                       | 10 %                             | -0.11                         | 0.10 | -0.06                         | 0.08 | -0.12                    | 0.13 |
| Mg                    | 0.01 %                           | 0.07                          | 0.06 | 0.04                          | 0.05 | 0.25                     | 0.07 |
|                       | 0.1 %                            | 0.15                          | 0.07 | 0.09                          | 0.05 | 0.39                     | 0.09 |
|                       | 1 %                              | 0.18                          | 0.13 | 0.09                          | 0.09 | 0.12                     | 0.15 |
|                       | 5 %                              | 0.21                          | 0.10 | 0.05                          | 0.09 | -1.19                    | 0.13 |
|                       | 10 %                             | 0.22                          | 0.12 | 0.13                          | 0.10 | 0.61                     | 0.15 |
| Cr                    | 0.01 %                           | 0.00                          | 0.05 | -0.02                         | 0.12 | -0.36                    | 0.13 |
|                       | 0.1 %                            | -0.09                         | 0.21 | -0.01                         | 0.12 | 0.72                     | 0.24 |
|                       | 1 %                              | -0.55                         | 0.17 | -0.19                         | 0.14 | 1.52                     | 0.22 |
|                       | 5 %                              | -1.09                         | 0.12 | -0.30                         | 0.06 | 4.51                     | 0.13 |

|    |         |       |      |        |        |       |      |
|----|---------|-------|------|--------|--------|-------|------|
|    | 10 %    | -1.32 | 0.19 | -0.37  | 0.09   | 5.36  | 0.21 |
| Rb | 0.1 %   | 0.03  | 0.04 | 0.04   | 0.04   | 0.63  | 0.06 |
|    | 1 %     | -0.01 | 0.06 | 0.01   | 0.06   | 0.34  | 0.09 |
|    | 5 %     | 0.03  | 0.04 | 0.01   | 0.07   | 0.01  | 0.08 |
|    | 10 %    | -0.03 | 0.09 | -0.05  | 0.10   | -0.67 | 0.13 |
|    | 0.1 %   | -0.05 | 0.17 | 0.01   | 0.11   | 0.66  | 0.20 |
| Ti | 1 %     | 0.13  | 0.17 | 0.06   | 0.14   | 0.01  | 0.22 |
|    | 2 %     | -0.18 | 0.13 | -0.06  | 0.05   | 0.56  | 0.14 |
|    | 5 %     | -0.39 | 0.12 | -0.12  | 0.06   | 1.44  | 0.13 |
|    | 10 %    | -0.46 | 0.15 | -0.13  | 0.11   | 1.86  | 0.18 |
|    | 0.001 % | 0.03  | 0.06 | -0.003 | -0.047 | -0.43 | 0.08 |
| Sr | 0.01 %  | 0.06  | 0.08 | 0.06   | 0.06   | 0.75  | 0.09 |
|    | 0.1 %   | 0.19  | 0.08 | 0.08   | 0.05   | -0.21 | 0.09 |
|    | 1 %     | -0.13 | 0.20 | -0.11  | 0.17   | -0.94 | 0.26 |