**Table S1.** Concentrations of Ca and Mg (in mg/kg) in the tufa samples recorded on Tablets P-14 (Piedra River), M-4 (Mesa River), RA-6 (Añamaza River) and RE-8 (Ebrón River) over time.

| | Ca | Mg | | Ca | Mg |
|---|---|---|---|---|---|
| **River Piedra. P-14** | | | **River Mesa. M-4** | | |
| Oct. 09–March 10 | 340,048.70 | 2896.50 | April 06–Sept. 06 | 336,502.56 | 3593.86 |
| April 09–Sept. 09 | 358,431.22 | 2624.81 | Oct. 05–March 06 | 357,815.76 | 3173.28 |
| Oct. 08–March 09 | 350,089.56 | 2072.37 | April 05–Sept. 05 | 356,389.23 | 2917.86 |
| April 08–Sept. 08 | 361,687.78 | 3014.51 | Oct. 04–March 05 | 349,247.79 | 2783.87 |
| Oct. 07–March 08 | 361,090.46 | 2063.65 | April 04–Sept. 04 | 360,772.29 | 2610.45 |
| April 07–Sept. 07 | 389,355.23 | 2901.14 | **River Añamaza. RA-6** | | |
| Oct. 06–March 07 | 385,578.08 | 1665.70 | Oct. 09–March 10 | 322,573.99 | 2138.19 |
| April 06–Sept. 06 | 372,343.36 | 2858.14 | April 09- Sept. 09 | 313,765.71 | 1279.57 |
| Oct. 05–March 06 | 389,001.42 | 2553.72 | Oct. 08–March 09 | 351,400.46 | 1620.27 |
| April 05–Sept. 05 | 399,244.27 | 2560.53 | April 08 –Sept. 08 | 358,784.09 | 1790.41 |
| Oct. 04–March 05 | 319,079.22 | 1696.76 | Oct. 07–March 08 | 355,859.79 | 1814.85 |
| April 04–Sept. 04 | 404,527.53 | 2645.89 | **River Ebrón. RE-8** | | |
| | | | Oct. 09–March 10 | 343,453.13 | 3236.91 |
| | | | April 09–Sept. 09 | 349,845.34 | 3643.50 |
| | | | Oct. 08–March 09 | 360,709.57 | 2799.35 |
| | | | April 08–Sept. 08 | 388,960.13 | 5155.07 |
| | | | Oct. 07–March 08 | 326,155.78 | 3910.71 |
| | | | Abril 07–Sept. 07 | 318,431.91 | 3745.74 |

**Table S2.** Hydrochemical characteristics of monitored sites in Piedra, Mesa, Añamaza and Ebrón Rivers. Concentrations in ppm.

| | Temp. (°C) | Conduct. (μS/cm) | pH | Alkalinity (as $HCO_3^-$) | Cl | $SO_4$ | Na | K | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|---|
| **River Piedra. P-14** | | | | | | | | | | |
| Oct. 09–March 10 | 10.1 | 465 | 8.41 | 202.33 | 15.50 | 29.81 | 6.94 | 3.47 | 65.20 | 13.06 |
| April 09–Sept. 09 | 16.2 | 673 | 7.98 | 260.91 | 15.60 | 134.77 | 8.69 | 3.69 | 88.20 | 27.58 |
| Oct. 08–March 09 | 8.0 | 680 | 8.06 | 270.86 | 10.10 | 108.53 | 6.33 | 1.64 | 78.40 | 25.78 |
| April 08–Sept. 08 | 14.5 | 578 | 8.03 | 260.36 | 11.20 | 79.10 | 5.24 | 2.77 | 83.70 | 20.43 |
| Oct. 07–March 08 | 9.0 | 705 | 7.83 | 281.24 | 15.20 | 106.78 | 8.30 | 1.81 | 93.30 | 28.56 |
| April 07–Sept. 07 | 16.1 | 676 | 8.16 | 256.67 | 17.60 | 102.77 | 7.22 | 2.48 | 79.40 | 27.15 |
| Oct. 06–March 07 | 9.3 | 686 | 8.08 | 270.35 | 14.10 | 102.48 | 6.62 | 2.77 | 79.30 | 29.13 |
| April 06–Sept. 06 | 17.9 | 676 | 8.35 | 268.37 | 12.60 | 88.23 | 7.89 | 2.44 | 81.10 | 27.65 |
| Oct. 05–March 06 | 7.9 | 689 | 7.15 | 291.17 | 19.30 | 104.24 | 6.80 | 1.67 | 84.30 | 27.30 |
| April 05–Sept. 05 | 18.4 | 663 | 8.18 | 266.27 | 25.30 | 100.42 | 7.11 | 2.25 | 78.50 | 28.28 |
| Oct. 04–March 05 | 12.4 | 667 | 7.85 | 263.32 | 18.20 | 108.98 | 6.72 | 1.75 | 89.10 | 25.58 |
| April 04–Sept. 04 | 17.8 | 624 | 8.31 | 261.84 | 21.00 | 88.22 | 6.25 | 1.90 | 82.00 | 24.37 |
| **River Mesa. M-4** | | | | | | | | | | |
| April 06–Sept. 06 | 14.5 | 716 | 8.27 | 279.61 | 47.8 | 39.19 | 35.63 | 2.25 | 65.90 | 20.83 |
| Oct. 05–March 06 | 8.0 | 807 | 8.51 | 300.93 | 80.0 | 78.38 | 45.52 | 2.49 | 87.70 | 21.93 |
| April 05–Sept. 05 | 17.1 | 742 | 7.59 | 288.97 | 90.1 | 68.56 | 44.06 | 2.90 | 84.20 | 21.95 |
| Oct. 04–March 05 | 10.8 | 637 | 7.98 | 266.80 | 36.2 | 62.28 | 19.72 | 2.64 | 80.10 | 20.24 |
| April 04–Sept. 04 | 14.4 | 611 | 7.50 | 264.23 | 39.7 | 60.81 | 20.63 | 2.17 | 71.90 | 20.33 |
| **River Añamaza. RA-6** | | | | | | | | | | |
| Oct. 09–March 10 | 10.4 | 8.49 | 717 | 227.47 | 24.50 | 210.52 | 16.6 | 6.08 | 144.6 | 18.11 |
| April 09- Sept. 09 | 16.2 | 8.35 | 745 | 225.76 | 9.22 | 207.20 | 4.85 | 4.00 | 120.10 | 21.62 |
| Oct. 08–March 09 | 8.5 | 7.98 | 840 | 244.28 | 10.90 | 231.43 | 7.63 | 4.43 | 128.2 | 21.49 |
| April 08 –Sept. 08 | 17.6 | 7.98 | 759 | 223.82 | 12.10 | 221.94 | 6.51 | 3.05 | 125.8 | 21.52 |
| Oct. 07–March 08 | 8.5 | 8.08 | 833 | 249.50 | 5.39 | 222.71 | 5.10 | 7.59 | 130.7 | 22.64 |
| **River Ebrón. RE-8** | | | | | | | | | | |
| Oct. 09–March 10 | 10.8 | 8.09 | 324 | 253.59 | 4.02 | 73.24 | 3.47 | 1.55 | 84.40 | 17.05 |
| April 09–Sept. 09 | 15.6 | 8.26 | 583 | 235.53 | 7.38 | 106.40 | 5.29 | 3.42 | 84.10 | 20.32 |
| Oct. 08–March 09 | 10.7 | 8.02 | 560 | 255.15 | 5.55 | 93.17 | 3.65 | 1.52 | 85.10 | 19.28 |
| April 08–Sept. 08 | 15.5 | 7.59 | 567 | 246.90 | 6.79 | 90.27 | 4.48 | 1.52 | 76.40 | 19.28 |
| Oct. 07–March 08 | 12.2 | 8.35 | 591 | 270.09 | 7.07 | 117.00 | 4.00 | 1.17 | 94.10 | 20.81 |
| Abril 07–Sept. 07 | 16.0 | 8.26 | 604 | 262.24 | 7.08 | 102.44 | 4.08 | 2.55 | 75.40 | 19.81 |

**Table S3.** Measured water ($T_w$), calculated $T_{Mg}$ (using $D_{Mg}$–T relationship in [45]) and calculated $T_{18O}$ (from $\delta^{18}O$ values in calcite and water, using the equation of [47]) temperatures for studied sites at Piedra, Mesa, Añamaza and Ebrón Rivers. We also present differences between the Mg-derived temperatures and measured water temperatures ($T_{Mg}$-$T_w$) and between $\delta^{18}O$-calculated temperatures and measured water temperatures ($T_{18O}$-$T_w$). All values are in °C.

| | $T_W$ | $T_{Mg}$ | $T_{18O}$ | $T_{Mg}$-$T_W$ | $T_{18O}$-$T_W$ |
|---|---|---|---|---|---|
| **River Piedra. P-14** | | | | | |
| Oct. 09–March 10 | 10.1 | 34.6 | 13.14 | 24.5 | 3.04 |
| April 09–Sept. 09 | 16.2 | 18.7 | 15.93 | 2.5 | −0.27 |
| Oct. 08–March 09 | 8.0 | 14.2 | 10.81 | 6.2 | 2.81 |
| April 08–Sept. 08 | 14.5 | 27.6 | 15.27 | 13.1 | 0.77 |
| Oct. 07–March 08 | 9.0 | 14.7 | 10.65 | 5.7 | 1.65 |

| | | | | | |
|---|---|---|---|---|---|
| April 07–Sept. 07 | 16.1 | 17.3 | 15.79 | 1.2 | −0.31 |
| Oct. 06–March 07 | 9.3 | 9.0 | 11.14 | −0.3 | 1.84 |
| April 06–Sept. 06 | 17.9 | 17.9 | 17.68 | 0.0 | −0.22 |
| Oct. 05–March 06 | 7.9 | 16.1 | 9.92 | 8.2 | 2.02 |
| April 05–Sept. 05 | 18.4 | 14.0 | 15.75 | −4.4 | −2.65 |
| Oct. 04–March 05 | 12.4 | 14.6 | 9.05 | 2.2 | −3.35 |
| April 04–Sept. 04 | 17.8 | 17.5 | 15.27 | −0.3 | −2.53 |
| **River Mesa. M-4** | | | | | |
| April 06–Sept. 06 | 14.5 | 27.3 | 14.0 | 12.8 | −0.5 |
| Oct. 05–March 06 | 8.0 | 28.7 | 17.2 | 20.7 | 9.2 |
| April 05–Sept. 05 | 17.1 | 25.3 | 14.7 | 8.2 | −2.4 |
| Oct. 04–March 05 | 10.8 | 25.5 | 11.3 | 14.7 | 0.5 |
| April 04–Sept. 04 | 14.4 | 20.5 | 14.9 | 6.1 | 0.5 |
| **River Añamaza. RA-6** | | | | | |
| Oct. 09–March 10 | 10.4 | 43.3 | 8.14 | 32.9 | −2.26 |
| April 09- Sept. 09 | 16.2 | 18.1 | 12.93 | 1.9 | −3.27 |
| Oct. 08–March 09 | 8.5 | 22.1 | 9.04 | 13.6 | 0.54 |
| April 08 –Sept. 08 | 17.6 | 23.5 | 14.15 | 5.9 | −3.45 |
| Oct. 07–March 08 | 8.5 | 23.7 | 8.57 | 15.2 | 0.07 |
| **River Ebrón. RE-8** | | | | | |
| Oct. 09–March 10 | 10.8 | 38.1 | 13.4 | 27.3 | 2.6 |
| April 09–Sept. 09 | 15.6 | 35.1 | 16.1 | 19.5 | 0.5 |
| Oct. 08–March 09 | 10.7 | 27.7 | 12.3 | 17.0 | 1.6 |
| April 08–Sept. 08 | 15.5 | 42.9 | 16.4 | 27.4 | 0.9 |
| Oct. 07–March 08 | 12.2 | 44.4 | 14.5 | 32.2 | 2.3 |
| Abril 07–Sept. 07 | 16.0 | 36.5 | 14.1 | 20.5 | −1.9 |

**Table S4.** Values of $\delta^{18}$ O and $\delta^{13}$ C (in ‰ VPDB) of tufa calcite recorded over time on Tablets P-14 (Piedra River), M-4 (Mesa River), RA-6 (Añamaza River) and RE-8 (Ebrón River).

| | $\delta^{18}$ $O_{calcite}$ ‰ VPDB | $\delta^{13}$ $C_{calcite}$ ‰ VPDB | | $\delta^{18}$ $O_{calcite}$ ‰ VPDB | $\delta^{13}$ $C_{calcite}$ ‰ VPDB |
|---|---|---|---|---|---|
| **River Piedra. P-14** | | | **River Mesa. M-4** | | |
| Oct. 09–March 10 | −7.67 | −8.12 | April 06–Sept. 06 | −8.37 | −8.53 |
| April 09–Sept. 09 | −8.33 | −8.62 | Oct. 05–March 06 | −9.26 | −9.02 |
| Oct. 08–March 09 | −7.94 | −7.56 | April 05–Sept. 05 | −8.54 | −8.68 |
| April 08–Sept. 08 | −8.22 | −8.47 | Oct. 04–March 05 | −7.89 | −8.75 |
| Oct. 07–March 08 | −8.20 | −7.52 | April 04–Sept. 04 | −8.57 | −9.16 |
| April 07–Sept. 07 | −8.28 | −8.59 | **River Añamaza. RA-6** | | |
| Oct. 06–March 07 | −8.17 | −7.64 | Oct. 09–March 10 | −8.20 | −7.00 |
| April 06–Sept. 06 | −8.34 | −9.01 | April 09- Sept. 09 | −8.60 | −7.10 |
| Oct. 05–March 06 | −8.09 | −7.34 | Oct. 08–March 09 | −8.00 | −7.50 |
| April 05–Sept. 05 | −8.29 | −8.58 | April 08 –Sept. 08 | −9.30 | −7.40 |
| Oct. 04–March 05 | −8.03 | −7.12 | Oct. 07–March 08 | −8.30 | −7.20 |
| April 04–Sept. 04 | −8.52 | −8.47 | **River Ebrón. RE-8** | | |
| | | | Oct. 09–March 10 | −7.84 | −7.26 |
| | | | April 09–Sept. 09 | −8.57 | −7.63 |
| | | | Oct. 08–March 09 | −7.76 | −6.93 |
| | | | April 08–Sept. 08 | −9.40 | −7.58 |
| | | | Oct. 07–March 08 | −8.82 | −7.60 |
| | | | Abril 07–Sept. 07 | −9.19 | −7.11 |

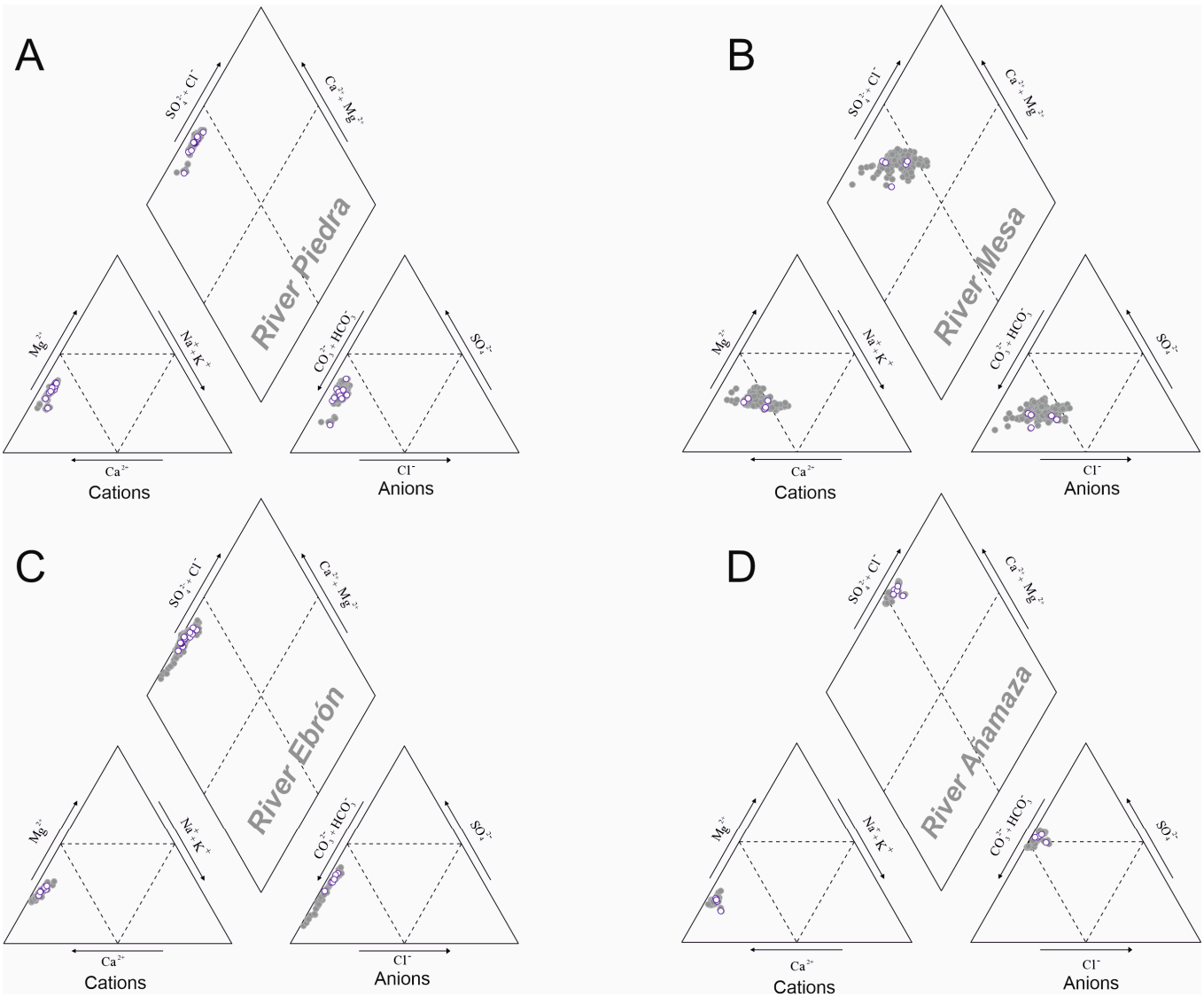


**Figure S1.** Piper diagrams for the waters of the Rivers (**A**) Piedra, (**B**) Mesa, (**C**) Ebrón and (**D**) Añamaza. Open circles correspond to water samples taken biannually in locations of studied tablets: from Warm 2004 to Cool 2009-2010 in River Piedra; from Warm 2004 to Warm 2006 in Mesa River; from Warm 2007 to Cool 2009-2010 in Ebron River; from Cool 2007-08 to cool 2009-10 in Amañaza River. Filled grey circles correspond to all available water samples obtained along the rivers in previous studies: Monasterio de Piedra Natural Park, from 1999 to 2012 [9]; Mesa River, from Warm 2003 to Warm 2009 [22]; Ebrón River, from Cool 2006-2007 to Cool 2009-2010 [21]; Añamaza River, from Warm 2007 to Cool 2009-2010 [23].

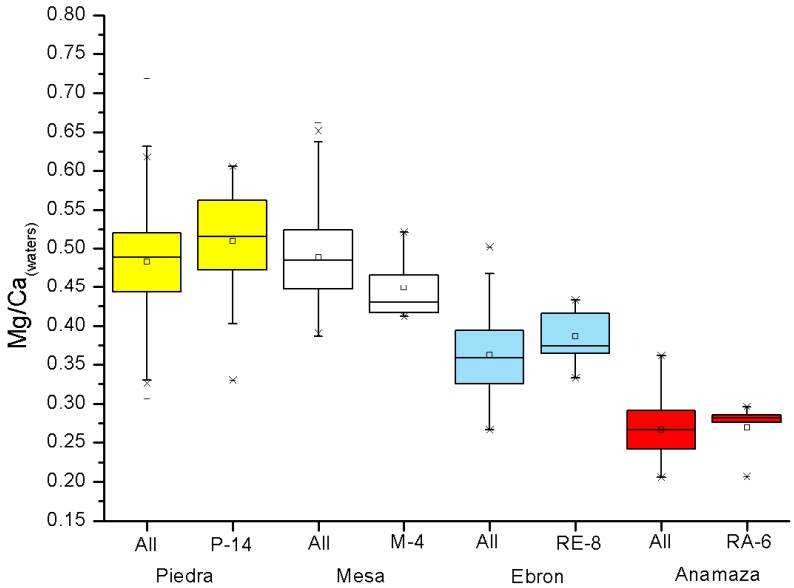


**Figure S2.** Box-and-whisker plots of the statistical distribution of Mg/Ca values in water samples biannually taken at studied sites in Piedra, Mesa, Ebron and Añamaza Rivers (P-14, M-4, RE-8 and RA-6, respectively) compared with the values of all available water samples obtained along rivers in previous studies: Monasterio de Piedra Natural Park, from 1999 to 2012 [19]; Mesa River, from Warm 2003 to Warm 2009 [22]; Ebrón River, from Cool 2006–2007 to Cool 2009–2010 [21]; Añamaza River, from Warm 2007 to Cool 2009–2010 [23]. The statistical measures plotted are the median (horizontal line inside box), 25th and 75th percentiles (bottom and top of the box, respectively), mean (square), 5th and 95th percentiles ("whiskers"), 1st and 99th percentiles (crosses) and maximum and minimum values (horizontal bars). Boxes for $Mg/Ca_{water}$ ratios at studied sites and boxes including data for all the sites along studied stretches of rivers show a certain degree of displacement, which is mainly related to locations of sites along the studied stretch. For example, Site P-14 along the Piedra River is located well downstream of the studied stretch, and tufa deposition is clearly active at the previous upstream sites [21]. The tufa calcite precipitation at these sites promotes successive increases in the Mg/Ca ratio of the downstream waters and then the presence of statistically higher $Mg/Ca_{water}$ ratios at Site P-14 with respect to the values for all the studied sites along the river. This situation also occurs in the Ebrón and Añamaza Rivers. In the Mesa River, the opposite occurs. The M4 site is located in the upstream part of the studied stretch, and it is not substantially affected by the previous tufa sedimentation processes. However, the downstream sites are progressively affected, promoting increments in the $Mg/Ca_{water}$ values. Furthermore, the important discharges of thermal waters at the end of the studied stretch of the Mesa River (Jaraba thermal springs with $Mg/Ca_{water}$ values of 0.6–0.7) also contributed to the statistically higher values found in the box representing all the studied stretches (see [22] for further details).

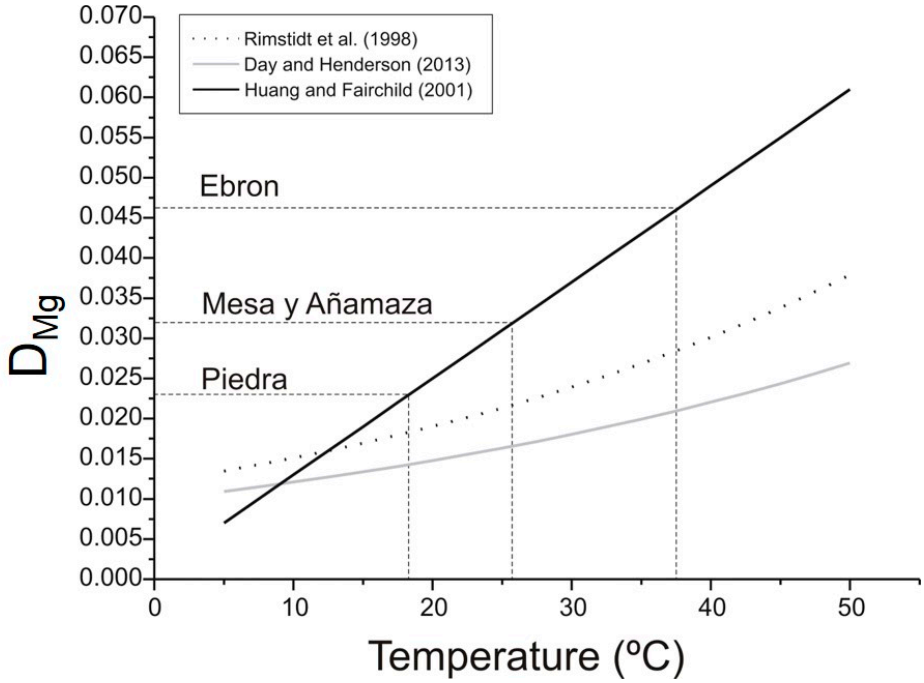


**Figure S3.** Experimental relationships between water temperature and magnesium partition coefficient $D_{Mg}$ determined in [45] and [46] under karst/speleothem-analogue conditions. $D_{Mg}$-T relationship from [45] between 15 and 25 °C, as adjusted in [3], corresponding to the equation:.

$$D_{Mg} = 0.0012 \times T + 0.001 \quad \text{(S1)}$$

whereas the results obtained in [46], which were between 7 and 35 °C, correspond to the equation:

$$\mathbf{D_{Mg}} = 0.0099 \times 10^{0.02T} \quad \text{(S2)}$$

In both cases, T is in °C.

For comparison, we also included the exponential best-fit curve to the data in [57] obtained in [46]:

$$D_{Mg} = 0.012 \times 10^{0.023T} \quad \text{(S3)}$$

We also indicate the average $D_{Mg}$ values for the tufas in the four rivers studied in this work and the corresponding temperatures obtained from the equation in [45] (S1).

The $D_{Mg}$-T trends from Equations S1 to S3 are substantially different, especially those empirically derived in [45] and [46] (S1 and S3, respectively). The calculated temperatures from the S2 and S3 equations for the studied tufas are exceedingly high, or in some cases, clearly out of the range of the experimental temperatures. Therefore, we only discuss the results obtained from Equation (S1), proposed in [45], in this work.

The calculated temperature using Equation S1 for the average $D_{Mg}$ value in the tufa from the Ebrón River was 37.4 °C, compared with the measured average temperature of 13.5 °C. For the tufas in the Mesa and Añamaza Rivers, the calculated temperatures were 25.5–26.1 °C, compared with the measured average temperatures (between 12.4 and 13 °C). The calculated temperature for the average $D_{Mg}$ value in the tufa from the Piedra River was 18 °C, whereas the measured average temperature was 13.1 °C. Overall, Equation S1 from the experimental data in [45] also predicted higher temperature values than the measured values but with differences among the studied rivers: the

average predicted temperatures in the Ebrón, Mesa and Añamaza Rivers were more than twice the measured values; however, for the Piedra River, they were only 5 °C higher (see text).