

Lithium isotopes and partition coefficients in inorganic carbonates: proxy calibration for weathering reconstruction

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Supplementary information

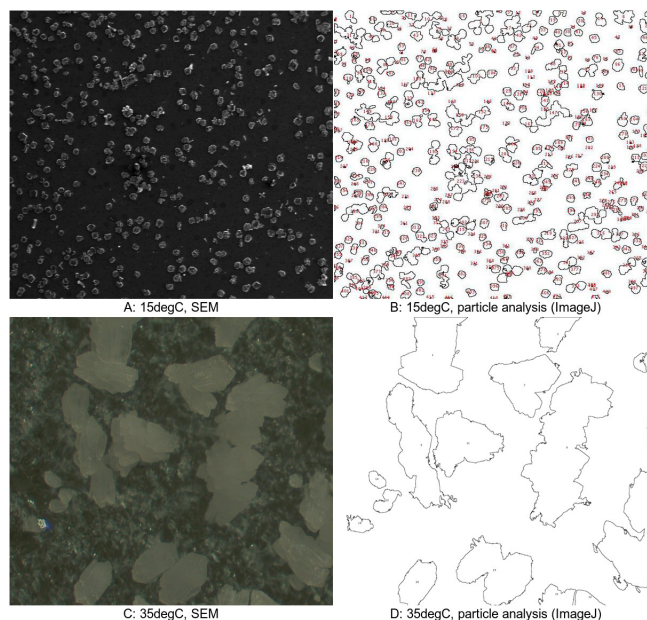


Figure 1: Example SEM and ImageJ images used for surface area estimates. **A:** SEM image of cave-analogue sample growth material at 15 °C. **B:** ImageJ-derived outlines of the crystals from SEM image A. **C:** SEM image of cave-analogue sample growth material at 35 °C. **D:** ImageJ-derived outlines of the crystals from SEM image C.

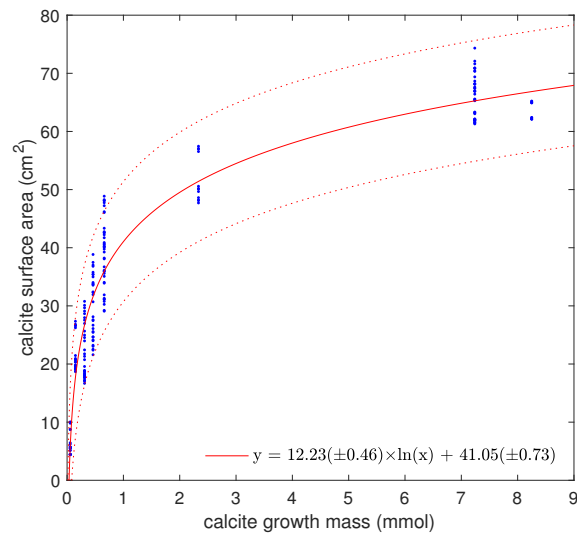


Figure 2: Relationship between the measured surface area of calcite growth crystals (cm^2) and the corresponding amount of calcite growth (mmol), as established using eight of our 7°C to 35°C experiments (each with a known growth mass). The surface area of calcite growth crystals is established using the method defined in section 2.6. For each experiment, nine or more values of the calcite surface area are defined using an array of images of the crystals on the plate. This provides us with a measure of variability of the surface area, due to factors such as heterogeneous crystal coverage. We use the Matlab curvefit function to fit a natural logarithmic relationship between growth mass and surface area. The resulting relationship ($y = 12.2(\pm 0.5) \times \ln(x) + 41.0(\pm 0.7)$) is used to define the calcite crystal surface area (and confidence interval) for any given calcite growth mass of our experiments.

| | T | pH ₀ | pH _t | DIC ₀ | DIC _t | 1000ln α | [Li] | [Mg] | [Co] | [Sr] | [Ba] | [Cd] |
|------------------|--------|-----------------|-----------------|------------------|------------------|-----------------|--------|--------|--------|--------|--------|-------|
| T | 1.0 | 0.1 | 0.9** | -0.8** | -0.8** | -0.9** | -0.7** | -0.8** | -0.8** | -0.8** | -0.7** | -0.6* |
| pH ₀ | 0.1 | 1.0 | 0.5 | 0.1 | 0.1 | -0.0 | -0.1 | -0.1 | -0.1 | -0.1 | -0.1 | 0.2 |
| pH _t | 0.9** | 0.5 | 1.0 | -0.6* | -0.6* | -0.8** | -0.5 | -0.7** | -0.7* | -0.7** | -0.7* | -0.4 |
| DIC ₀ | -0.8** | 0.1 | -0.6* | 1.0 | 1.0** | 0.8** | 0.9** | 0.9** | 0.9** | 0.9** | 0.9** | 0.5 |
| DIC _t | -0.8** | 0.1 | -0.6* | 1.0** | 1.0 | 0.8** | 1.0** | 0.9** | 0.9** | 0.9** | 0.9** | 0.5 |
| 1000ln α | -0.9** | -0.0 | -0.8** | 0.8** | 0.8** | 1.0 | 0.7** | 0.8** | 0.8** | 0.9** | 0.8** | 0.6* |
| [Li] | -0.7** | -0.1 | -0.5 | 0.9** | 1.0** | 0.7** | 1.0 | 0.9** | 0.9** | 0.9** | 0.9** | 0.4 |
| [Mg] | -0.8** | -0.1 | -0.7** | 0.9** | 0.9** | 0.8** | 0.9** | 1.0 | 0.9** | 1.0** | 0.9** | 0.5 |
| [Co] | -0.8** | -0.1 | -0.7* | 0.9** | 0.9** | 0.8** | 0.9** | 0.9** | 1.0 | 1.0** | 1.0** | 0.5 |
| [Sr] | -0.8** | -0.1 | -0.7** | 0.9** | 0.9** | 0.9** | 0.9** | 1.0** | 1.0** | 1.0 | 1.0** | 0.5 |
| [Ba] | -0.7** | -0.1 | -0.7* | 0.9** | 0.9** | 0.8** | 0.9** | 0.9** | 1.0** | 1.0** | 1.0 | 0.5 |
| [Cd] | -0.6* | 0.2 | -0.4 | 0.5 | 0.5 | 0.6* | 0.4 | 0.5 | 0.5 | 0.5 | 0.5 | 1.0 |

Table 1: Spearman’s rank correlation coefficients (ρ) between parameters measured in the solution and 1000ln α , at all temperatures. Correlation coefficients marked with ‘*’ denote cases with $0.01 < \rho \leq 0.05$. Correlation coefficients marked with ‘**’ denote cases with $\rho \leq 0.01$. Column pH₀ uses the measured pH in the initial solution. Column pH_t uses the calculated pH after 30 seconds of CO₂ degassing and the corresponding increase in pH calculated using rate constants from Dreybrodt and Scholz (2011). Column DIC₀ uses the calculated amount of DIC in our solution using PHREEQC. Column DIC_t is DIC₀ minus the excess CO₂, 95% of which is expected to have outgassed from our thin film solution within a maximum of 12 seconds (Dreybrodt, 2012). More focussed experiments are required to narrow down specific causes of variation in 1000ln α .

| | T | Growth Rate | 1000ln α | [Li] | [Mg] | [Co] | [Sr] | [Cd] | [Ba] |
|-----------------|--------|-------------|-----------------|--------|--------|-------|--------|--------|--------|
| T | 1.0 | 0.8* | -0.8** | -0.9** | -0.5 | -0.7* | -0.9** | 0.8** | -1.0** |
| Growth Rate | 0.8* | 1.0 | -0.8* | -1.0** | -0.9** | -0.8* | -0.5 | 0.5 | -0.6 |
| 1000ln α | -0.8** | -0.8* | 1.0 | 0.7** | 0.5 | 0.5 | 0.7** | -0.7** | 0.7** |
| [Li] | -0.9** | -1.0** | 0.7** | 1.0 | 0.6* | 0.7** | 0.9** | -0.7** | 0.9** |
| [Mg] | -0.5 | -0.9** | 0.5 | 0.6* | 1.0 | 0.4 | 0.3 | -0.6* | 0.3 |
| [Co] | -0.7* | -0.8* | 0.5 | 0.7** | 0.4 | 1.0 | 0.8** | -0.3 | 0.8** |
| [Sr] | -0.9** | -0.5 | 0.7** | 0.9** | 0.3 | 0.8** | 1.0 | -0.8** | 1.0** |
| [Cd] | 0.8** | 0.5 | -0.7** | -0.7** | -0.6* | -0.3 | -0.8** | 1.0 | -0.7** |
| [Ba] | -1.0** | -0.6 | 0.7** | 0.9** | 0.3 | 0.8** | 1.0** | -0.7** | 1.0 |

Table 2: Spearman’s rank correlation coefficients (ρ) between parameters measured in precipitated calcite and 1000ln α . Correlation coefficients marked with ‘*’ denote cases with $0.01 < \rho \leq 0.05$. Correlation coefficients marked with ‘**’ denote cases with $\rho \leq 0.01$. Column ‘GR’ denotes modelled growth rate in units of 10^{-8} mmol cm⁻² s⁻¹.

Bibliography

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