(2008).

Determination of equilibrium Ca isotope fractionation between calcite and water using pressure solution and a laboratory compaction column

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Calcium isotope measurements have been broadly applied to low-temperature and high-temperature geochemistry[1], particularly in calcite-fluid interactions. Nevertheless, equilibrium fractionation factor between calcite and water remains unclear. Observations based on deep sea carbonate pore fluids have been used to argue that $\Delta^{44}Ca_{eq}$ (or $1000\ln\alpha_{calcite-water}$) is between 0‰ and -0.5‰ near room temperature[2,3], a large uncertainty in comparison to typical variations of 1~2‰ in $\delta^{44}Ca$. Laboratory precipitation experiments show a similarly wide range, and suffer from the difficulty of precipitating calcite near equilibrium[4].

We developed a flow-through compaction apparatus to measure pressure solution and strain rates in calcite grain packs and are now using it to constrain $\Delta^{44}Ca_{eq}$ for calcite precipitation. We use Sr/Ca and $^{87}Sr/^{86}Sr$ measured in pre-equilibrated fluid flowing slowly through a small column (0.01 ml/min, 2 cm^3 column volume) to estimate the calcite-fluid precipitation and dissolution rates. Sieved calcite grains (90-212μm) were compacted with confining pressure of 10 MPa and axial stress of 5 MPa. Bulk dissolution rates measured with $^{87}Sr/^{86}Sr$ are approximately equal to precipitation rates measured with Sr/Ca and are in the range 10^{-10} to 2×10^{-8} mol/m^2/s^{-1}. Dissolution occurs at higher rates mainly on the grain-grain contacts, which are at elevated pressure due to the axial stress and limited surface area. Precipitation occurs in the open pore space where there is abundant calcite surface area, so is likely to occur at close-to-equilibrium conditions. The dissolved Ca in the input solution is not in isotopic equilibrium with the solid but can reach steady state "equilibrium" before exiting the column when reaction rates are fast enough. We can plot apparent $\Delta^{44}Ca$ vs reaction rate and approach the equilibrium value from the low and high side with different input $\delta^{44}Ca$ to evaluate the likely range of equilibrium values. Results from 4 experiments indicate that $\Delta^{44}Ca_{eq}$ is -0.25 ± 0.10‰. Precipitation rates are of order 10^{-9} mol/m^2/s or slower.

1. DePaolo, D. J. *Rev. Mineral. Geochemistry* 55, 255–288 (2004).
2. Fantle, M. S. & DePaolo, D. J. *GCA* 71, 2524–2546 (2007).
3. Bradbury, H.J. and Turchyn, A.V., *GCA*, 236, 121-139 (2018)
4. Jacobson, A. D. & Holmden, C. *EPSL* 270, 349–353