

GRANTEE: CALIFORNIA INSTITUTE OF TECHNOLOGY
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TITLE: Isotope Tracer Studies of Diffusion in Silicates and of Geological
Transport Processes Using Actinide Elements

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FINAL REPORT

Objectives: The objectives were directed toward understanding the transport of chemical species in nature, with particular emphasis on aqueous transport in solution, in colloids, and on particles. Major improvements in measuring ultra-low concentrations of rare elements were achieved. We focused on two areas of studies: 1) Field, laboratory, and theoretical studies of the transport and deposition of U, Th isotopes and their daughter products in natural systems; and 2) Study of calcium isotope fractionation effects in marine carbonates and in carbonates precipitated in the laboratory, under controlled temperature, pH, and rates of precipitation.

Project Results: A major study of isotopic fractionation of Ca during calcite growth from solution has been completed and published. It was found that the isotopic shifts widely reported in the literature and attributed to biological processes are in fact due to a small equilibrium fractionation factor that is suppressed by supersaturation of the solution. These effects were demonstrated in the laboratory and with consideration of the solution conditions in natural systems, where $[Ca^{2+}] \gg [CO_3^{2-}] + [HCO_3^-]$. The controlling rate is not the diffusion of Ca, as was earlier proposed, but rather the rate of supply of $[CO_3^{2-}]$ ions to the interface. This now opens the issues of isotopic fractionation of many elements to a more physical-chemical approach. The isotopic composition of Ca $\Delta(^{44}Ca/^{40}Ca)$ in calcite crystals has been determined relative to that in the parent solutions by TIMS using a double spike. Solutions were exposed to an atmosphere of NH_3 and CO_2 , provided by the decomposition of $(NH_4)_2CO_3$. Alkalinity, pH, and concentrations of CO_3^{2-} , HCO_3^- , and CO_2 in solution were determined. The procedures permitted us to determine $\Delta(^{44}Ca/^{40}Ca)$ over a range of pH conditions, with the associated ranges of alkalinity. Two solutions with greatly different Ca concentrations were used, but, in all cases, the condition $[Ca] \gg [CO_3^{2-}]$ was met. A wide range in $\Delta(^{44}Ca/^{40}Ca)$ was found for the calcite crystals, extending from 0.04 ± 0.13 to -1.34 ± 0.15 ‰, generally anti-correlating with the amount of Ca removed from the solution. The results show that $\Delta(^{44}Ca/^{40}Ca)$ is a linear function of the saturation state of the solution with respect to calcite (Ω). The two parameters are very well correlated over a wide range in Ω for each solution with a given $[Ca]$. Solutions, which were vigorously stirred, showed a much smaller range in $\Delta(^{44}Ca/^{40}Ca)$ and gave values of -0.42 ± 0.14 ‰, with the largest effect at

low Ω . It is concluded that the diffusive flow of CO_3^{2-} into the immediate neighborhood of the crystal-solution interface is the rate-controlling mechanism and that diffusive transport of Ca^{2+} is not a significant factor. The data are simply explained by the assumptions that: a) the immediate interface of the crystal and the solution is at equilibrium with $\Delta(^{44}\text{Ca}/^{40}\text{Ca}) \sim -1.5 \pm 0.25 \text{ ‰}$, and b) diffusive inflow of CO_3^{2-} causes supersaturation, thus precipitating Ca from the regions, exterior to the narrow zone of equilibrium. We consider this model to be a plausible explanation of the available data reported in the literature. The well-resolved but small and regular isotope fractionation shifts in Ca are thus not related to the diffusion of very large hydrated Ca complexes, but rather due to the ready availability of Ca in the general neighborhood of the crystal-solution interface. The largest isotopic shift which occurs is a small equilibrium effect which is then subdued by supersaturation precipitation for solutions where $[\text{Ca}^{2+}] \gg [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$. It is shown that there is a clear temperature dependence of the net isotopic shifts, which is simply due to changes in Ω , due to the equilibrium "constants" dependence on temperature, which changes the degree of saturation and hence the amount of isotopically unequilibrated Ca precipitated. The effects that are found in natural samples, therefore, will be dependent on the degree of diffusive inflow of carbonate species at or around the crystal-liquid interface in the particular precipitating system, thus limiting the equilibrium effect.

The second study treats the problem of Sr isotopic changes in aquifer waters in carbonate terrains. It was found that while dolomite dissolution, calcite precipitation, and clay exchange may govern the bulk chemistry of such waters, the major source of Sr is from the dissolution of the minor phase anhydrite. A theoretical model was presented that showed that the coupling of intrinsic reaction rates of the participating phases, the concentration of Sr in these phases and the modal abundances of the mineral phases are the key parameters. Large amounts of anhydrite or clays are not at all required to provide the bulk contributions found in solution. The approach laid out in this study has broad implications in problems relating to understanding and modeling of element abundances in groundwater.

Publications:

D. Lemarchand, G. J. Wasserburg and D. A. Papanastassiou (2004) Rate-controlled calcium isotope fractionation in synthetic calcite. *Geochim. Cosmochim. Acta*, Vol. 68, No. 22, pp. 4665-4678.

D. Jacobson and G. J. Wasserburg (2005) Anhydrite and the Sr isotope evolution of groundwater in a carbonate aquifer. *Chemical Geology*, Vol. 214, pp. 331-350.

J. Viers and G. J. Wasserburg (2004) Behavior of Sm and Nd in a lateritic soil profile. *Geochim. Cosmochim. Acta*, Vol. 68, No. 9, pp. 2043-2054.