



Stable oxygen isotope fractionation during inorganic precipitation of calcite: Effect of precipitation rate and pH

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Stable oxygen isotope fractionation during inorganic calcite formation was experimentally studied by spontaneous precipitation at various pH ($8.3 < \text{pH} < 10.5$), precipitation rates ($1.8 < \log R < 4.4 \mu\text{mol/m}^2/\text{h}$) and temperatures (5° , 25° , and 40°C) using the CO_2 diffusion technique. The results show that the apparent stable oxygen isotope fractionation factor between calcite and water, $\alpha(\text{calcite-water})$, was influenced by the pH of the solution and the precipitation rate of calcite. At a constant temperature and similar precipitation rates, $1000\ln(\alpha(\text{calcite-water}))$ decreases with increasing pH of the solution. If the temperature and pH are constant, $1000\ln(\alpha(\text{calcite-water}))$ decreases with elevated precipitation rates of calcite. Our results indicate that a reliable temperature-dependence of $1000\ln(\alpha(\text{calcite-water}))$ within the range from 5 to 40°C can only be obtained if both pH and precipitation rate are known. The slope of $1000\ln(\alpha(\text{calcite-water}))$ versus temperature generally increases with decreasing precipitation rate at constant pH. In comparison to the equilibrium oxygen isotope fractionation between calcite and water from previous literature, which are based on experimental studies or theoretical calculations, most of our experimental data show less oxygen isotope fractionation. However, the negatively rate-controlled $1000\ln(\alpha(\text{calcite-water}))$ values obtained by our experiments indicate that equilibrium oxygen isotopic fractionation factor calcite-water chosen by the previous literature might be problematic. The "true" equilibrium $\alpha(\text{calcite-water})$ values should be slightly but systematically higher than those proposed by Kim and

O'Neil [Kim S.-T. and O'Neil J.R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* 61, 3461-3475].