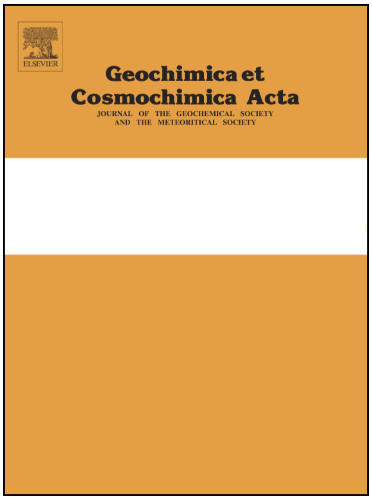

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Calcium and Strontium Isotope Fractionation in Aqueous Solutions as a Function of Temperature and Reaction Rate; I. Calcite

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Abstract: In order to study Strontium (Sr) partitioning and isotope fractionation of Sr and Calcium (Ca) in calcite we performed precipitation experiments decoupling temperature and precipitation rate (R*). Calcite was precipitated at 12.5, 25.0 and 37.5 °C by diffusing NH_3 and CO_2 gases into aqueous solutions closely following the experimental setup of Lemarchand et al (2004). The precipitation rate (R*) for every sample was determined applying the initial rate method and from the specific surface area of almost all samples for each reaction. The order of reaction with respect to Ca^{2+} ions was determined to be one and independent of T. However, the order of reaction with respect to HCO_3^- changed from three to one as temperature increases from 12.5, 25 °C and 37.5 °C. Strontium incorporated into calcite (expressed as D_{Sr}= $[Sr/Ca]_{calcite}$/ $[Sr/Ca]_{solution}$) was found to be R* and T dependent. As a function of increasing R* the $\Delta^{88/86}$Sr-values become more negative and as temperature increases the $\Delta^{88/86}$Sr values also increase at constant R*. The D_{Sr} and $\Delta^{88/86}$Sr-values are correlated to a high degree and depend only on R* being independent of temperature, complexation and varying initial ratios. Latter observation may have important implications for the study of diagenesis, the paleo-sciences and the reconstruction of past environmental conditions. Calcium isotope fractionation ($\Delta^{44/40}$Ca) was also found to be R* and T dependent. For 12.5 and 25.0 °C we observe a general increase of the $\Delta^{44/40}$Ca values as a function of R* (Lemarchand et al type behavior, Lemarchand et al (2004)). Whereas at 37.5 °C a significant decreasing $\Delta^{44/40}$Ca is observed relative to increasing R* (Tang et al type behavior, Tang et al. (2008)). In order to reconcile the discrepant observations we suggest that the temperature triggered change from a Ca^{2+}-NH_3-aquacomplex covalent controlled bonding to a Ca^{2+}-H_2O-aquacomplex van-der-Waals controlled bonding caused the change in sign of the R* - $\Delta^{44/40}$Ca slope due to the switch of an equilibrium type of isotope fractionation related to the covalent bonding during lower temperatures to a kinetic type of isotope fractionation at higher temperatures. This is supported by the observation that the $\Delta^{44/40}$Ca ratios are independent from the [Ca] : [DIC] ratio at 12.5 and 25°C but highly dependent at 37.5°C. Our observations imply the chemical fluid composition and temperature dependent complexation controls the amount and direction of Ca isotope fractionation in contrast to the Sr isotopes which do not show any change of its fractionation behaviour as a function of complexation in the liquid phase.