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Effect of the growth rate on Cu^{2+} incorporation into calcite and aragonite

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The presence of trace cations in carbonate minerals that readily form on Earth's surface environments can provide insights on the composition and parameters of the precipitating solution (e.g. temperature, growth rate, precursor phases). These informations are essential for the reconstruction of the (paleo)environmental conditions occurring at the time of mineral formation, given that the mechanisms controlling the incorporation of an individual foreign ion in a mineral structure are known and quantified. In this study, the incorporation of Cu^{2+} in both calcite and aragonite was experimentally explored at a wide range of mineral growth rates ($\sim10^{-9} < r_p < 10^{-7}$ mol/m²/s) on synthetic seed crystals using the constant addition technique in mixed flow reactors at 25°C and 1 bar $p\mathrm{CO}_2$. The obtained results show that during co-precipitation of Cu^{2+} with calcite, $D_{Cu,calcite}$ (i.e., distribution coefficient) values are > 1 and decrease with increasing growth rate. In contrast, $D_{Cu,aragonite}$ values are < 1 and increase with increasing growth rate. As both calcite and aragonite D_{Cu} exhibit a strong dependency on r_p and on the saturation state of the solution, it suggests that the Cu/Ca ratio of both phases is strongly controlled by these two parameters. While the incorporation of Cu^{2+} into calcite implies the formation of a dilute solid-solution between calcite and $CuCO_3$, it appears that the incorporation of Cu^{2+} into aragonite is related to the availability of defect sites at the growing mineral surface.