# Effect of amino acids on the growth kinetics and Ca isotopic composition of gypsum

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Stirred gypsum ($CaSO_4 \cdot 2H_2O$) precipitation experiments (initial saturation state = 2.3, duration ≈ 1h) were conducted in the presence of glycine (190 $\mu$M), L-alanine (190 $\mu$M), D- and L-arginine (45 $\mu$M), and L-tyrosine (200 $\mu$M) to investigate the effect of simple organic compounds on the kinetics and the Ca isotopic composition of the resultant minerals. Relative to abiotic controls, glycine, tyrosine, and alanine inhibited precipitation rates by ~10, 27, and 29%, respectively, while L- and D-arginine accelerated crystal growth by ~25 and 70%, respectively. With the exception of tyrosine, amino acid induced inhibition resulted in crystals with $\Delta^{44}Ca$ values ~0.3‰ lower than the control ($\Delta^{44}Ca = \delta^{44}Ca_{solid} - \delta^{44}Ca_{fluid}$). In contrast, crystals from the tyrosine and D- and L-arginine experiments had similar $\Delta^{44}Ca$ values as the controls. The solution in all experiments lost 70% of $Ca_{(aq)}$ to the solid, making them comparable to previous abiotic experiments [1]. Growth inhibition by glycine, alanine and tyrosine is most likely due to the difference between the pI of the amino acids and the gypsum surface. At the pH of the growth solution (~5.7), the amino acids have a net negative charge whereas the gypsum surface ($P_{ZNC} = 7.5$) has a net positive charge, creating an electrostatic gradient that induces attachment between the amino acid and the surface. By contrast, arginine has a net positive charge in solution, which precludes attachment. *Ab initio* molecular modelling of the (010), (-111), (110), (120), and (011) faces suggests that glycine inhibits growth by binding to Ca sites on the crystal surface via the deprotonated carboxylic group. We suggest that the binding of glycine and alanine to the gypsum surface increases the energetic barrier of $Ca^{2+}$ adsorption on the growing surface, thus inducing an isotopic fractionation effect. The proposed mechanism may be relevant to biogenic marine calcite, given the range of organic molecules found in sea water with deprotonated functional groups, potentially contributing to the isotopic composition of foraminiferal tests and nannofossils.

[1] Harouaka et al. (2014); *GCA*; **129** 157