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

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Gypsum precipitation experiments were conducted in the presence of S oxidizing microbes in order to determine the existence of a biological Ca isotopic signature. Results indicated that the presence of microbes retards precipitation rate relative to an abiotic negative control, and that the $\delta^{44/42}$Ca of the biotic crystals were ~0.4‰ lighter than the control crystals. The observed behaviour may be explained by the inhibition of gypsum growth by organic molecules produced during cellular metabolism and growth. To explore this hypothesis, abiotic gypsum precipitation experiments were carried out in the presence of the amino acids glycine, and the D and L enantiomers of arginine, and compared to a previous abiotic study [1]. Precipitation rates were inhibited by glycine, L-arginine, and D-arginine by 56, 38, and 30%, respectively, relative to a control. Nucleation rates were inhibited by glycine and D-arginine by 41 and 36%, respectively, but were accelerated by L-arginine by 34%. Inhibition in both nucleation and precipitation rates suggests that amino acids retard growth by adsorption onto active surface sites [2] as well as the complexation of free Ca^{2+} in solution prior to nucleation. The creation of a complexed Ca reservoir has been hypothesized to produce a detectable isotopic effect (~0.3‰) in the precipitates [1], and could thus be a viable mechanism for biologically induced isotopic fractionation. The opposing effects of D and L arginine on nucleation suggest that if such an isotope effect exists, it could be chiral specific.

[1] Harouaka, Eisenhauer, Fantle (2013) *GCA* doi 10.1016/j.gca.2013.12.004 [2] Hamdona, Hadad (2008) *Desalination* **228** 277-286