



Building amorphous calcium carbonate into geochemical biomineralisation models

David Evans¹, William Gray², James Rae³, Rosanna Greenop³, Paul Webb⁴, Kirsty Penkman⁵, Roland Kröger⁶, and Nicola Allison³

¹Institute for Geosciences, Goethe University Frankfurt, Germany (evans@em.uni-frankfurt.de)

²Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), Gif-sur-Yvette, France

³School of Earth and Environmental Sciences, University of St Andrews, St Andrews, UK

⁴School of Chemistry, University of St Andrews, St Andrews, UK

⁵BioArCh, Department of Chemistry, University of York, York, UK

⁶Department of Physics, University of York, York, UK

Amorphous calcium carbonate (ACC) has been observed, or inferred to exist, in the majority of the major phyla of marine calcifying organisms. The CaCO₃ produced by these organisms represents one of the largest long-term carbon sinks on Earth's surface, such that identifying how calcification will respond to anthropogenic climate change is an urgent priority. A substantial portion of our knowledge of the biomineralisation process of these organisms is derived from inferences based on skeletal geochemical data, yet such models typically do not include an ACC component because little is known about trace element and isotope fractionation into ACC. In order to address this, we present, to our knowledge, the first structural and geochemical data of ACC precipitated from seawater under varying carbonate system conditions, seawater Mg/Ca ratios, and in the presence of three of the most common intracrystalline amino acids (aspartic acid, glutamic acid, and glycine). Based on these data we identify the carbonate system conditions necessary to produce ACC from seawater [Evans *et al.*, 2019], and identify the dominant controls on ACC geochemistry. As an example, we utilise these data to build a simple biomineralisation model for the low-Mg (e.g. planktonic) foraminifera, based on precipitation of low-Mg calcite through an ACC precursor phase in a semi-enclosed pool. This exercise demonstrates that the observed shell geochemistry of this group of organisms can be fully reconciled with a model that includes an ACC component, and moreover that constraints can be placed on the degree of ACC utilisation and the ACC-calcite transformation process. More broadly, the exercise demonstrates that knowledge of the characteristics and geochemistry of ACC is important in the development of a process-based understanding of marine calcification.

Evans, D., Webb, P., Penkman, K. Kröger, R., & Allison, N. [2019] The Characteristics and Biological Relevance of Inorganic Amorphous Calcium Carbonate (ACC) Precipitated from Seawater. *Crystal Growth & Design* **19**: 4300.