Understanding cold-water coral strength: Molecular interactions and scaling simulations

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Abstract

1. Introduction

Cold-water coral reefs provide essential services to marine ecosystems. However, they face significant threats by ocean acidification, rising temperatures, or deoxygenation. Their ecosystem services are enabled through formation of powerful and efficient material architectures making up a mineralised skeleton. Cold-water corals form these mineralised skeletons in extreme environments that are characterized by low temperatures, high pressures, and limited resources. They form a material architecture that uses aragonite (CaCO) as crystalline building block (1). While aragonite single crystals exhibit very high stiffness and strength (1-7), polycrystalline material they form in a tightly controlled biofabrication process exhibits a much lower but still exceptional strength – up to ten times stronger than concrete (1). Interestingly this strength is retained even when skeletons are synthesised in adverse oceanic conditions while stiffness is not and it is currently unclear why this is the case (1). The change in mechanical properties along the length scales of the material architecture implies a structure-property relationship that may provide answers why strength is maintained.

Interfaces, i.e., surfaces where aragonite grains interact with each other or with proteins, have been identified as critical failure points in the material architecture (1). However, how these interfaces moderate the structure-property relationship is unclear and difficult to assess experimentally. Therefore, the aim of this study was to investigate these interfaces to understand its role in the structure-property relationship of the polycrystalline skeletal material. To do so our objectives were: (i) explore the interactions between aragonite crystals and organic proteins; (ii) integrate coral acid-rich proteins (CARPs) to model crystal-protein interfaces and analyse their effect on mechanical properties; (iii) employ multiscale coarse-graining techniques to simulate larger material compartments

2. Methods

We use molecular dynamics (MD) simulations to investigate crystal-protein interaction. We refine existing interatomic potentials for aragonite (8) to improve modelling accuracy using GULP (9) for parameter optimisation. We incorporated a representation of CARPs, such as Lustrin A (1L3Q) (10) and aragonite protein-7 (2JYP) (11) to represent crystal-protein interfaces and analyse their effect on mechanical properties. Using these refined potentials,

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we simulate interfaces between aragonite and proteins, incorporating structures prepared with CHARMM-GUI (12) for seamless integration into MD simulations in LAMMPS (13). CARPs are relaxed, equilibrated and shaped via steered MD before being interfaced with aragonite This approach allows us to accurately capture the behaviour of these interfaces, providing insights into the role of organic components in coral structures.

Another factor contributing to reduced mechanical properties is intracrystalline porosity. We introduce nanoporosity (1-2 nm) using a custom Python script that preserves electroneutrality. Porosity levels up to 3.5% to 4% are tested, representing the maximum levels permitted by Coulombic interactions.

To address the limitations of MD, we use multiscale coarse-graining (MSCG) (14). The method maps groups of atoms to single beads, simplifying complex systems while retaining essential interactions. Interaction potentials are fitted using force-matching techniques. To bridge the gap between molecular-scale simulations and experimentally observed mechanical properties, we aim to eventually scale up our models to simulate the behaviour of entire coral skeletons. Thus, the data obtained at smaller scale is to be used as input for coarser-scale simulations.

3. Results

Single crystals of aragonite simulated using MD with refined potentials demonstrate good agreement with both experimental and previous simulation results on stiffness tensors, showing deviations within 10% (1). Additionally, investigations into twin interfaces reveal that crystal-crystal misorientation does not significantly reduce mechanical strength, indicating that twin boundaries are stable structures, in contrast to low-angle grain boundaries (15). Furthermore, the introduction of CARPs at the interface significantly diminishes strength, with tensile testing revealing a reduction to approximately 700 MPa compared to the 4-6 GPa typically observed in single crystals, highlighting the influence of organic-inorganic interactions. Lastly, simulations suggest that nanopores minimally impact mechanical properties, particularly when compared to the effects of larger intercrystalline pores observed experimentally.

4. Discussion

We here investigated the interfaces in the polycrystalline skeletal material used by cold-water corals to form their skeleton. By combining refined MD simulations with multiscale coarse-graining, we revealed mechanisms behind the length scale dependent mechanical properties of coral skeletons. We demonstrate that interfaces, particularly crystal-protein interactions, are key to understanding the change in mechanical properties along the material architecture. Our research may help to challenge existing experimental data on the mechanical properties of polycrystalline coral skeletons (1) and help to uncover the structure-property relationship of this material architecture. This, in turn, may be useful for the biomimetic design of new materials.

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