

Peptoid-enhanced Mineralization of CaCO₃

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Abstract: In nature, living organisms use peptides and proteins to precisely control the nucleation and growth of inorganic minerals and sequester CO₂ *via* mineralization of CaCO₃. Here, we report the exploitation of a novel class of sequence-specific non-natural polymers called peptoids as catalysts to accelerate the calcite crystal growth. We identified peptoids composed of hydrophobic and anionic monomers that exhibit both a high degree of morphological control of CaCO₃ mineralization, and a 25-fold increase in the levels of calcite growth acceleration. Existing organic calcite accelerants show acceleration rates of only 1.5 fold. These findings provide a guideline to develop robust sequence-specific non-natural polymers to mimic the functions of natural peptides or proteins toward the mineralization of CaCO₃, and use them as catalysts to sequester CO₂ through the conversion of CO₂ to CaCO₃ minerals.

Background

It is generally believed that CO₂ emissions are the most important cause of global warming. Therefore, developing new materials which can efficiently capture CO₂ and reduce atmospheric CO₂ concentration has drawn a great amount of attention.¹⁻² Currently, many types of materials have been developed and used for targeting CO₂ capture. For example, amine solution was used for chemisorption of CO₂,³ and porous materials (e.g. zeolites,⁴ metal-organic frameworks^{1,5}) were developed for physical adsorption of CO₂. While many intensive studies have focused on developing new materials for either chemical absorptions or physical absorption of CO₂, another promising alternative for CO₂ capture is the use of catalysts to accelerate the CO₂ mineralization,⁶ in which the CO₂ is converted into thermodynamically stable carbonate minerals and permanently stored in solid form. Therefore, development of catalysts for CO₂ mineralization will be significantly important.

In nature, living organisms sequester significant amount of CO₂ through a biomineralization process in an energy efficient way to produce well-defined CaCO₃ minerals for routine functions (e.g. mechanical support, protection), in which the proteins can induce or accelerate precipitation of CaCO₃ - both crystalline and amorphous - from aqueous precursors.⁶⁻⁸ In vitro experiments have demonstrated that these same proteins, as well as shorter chain peptides that mimic certain regions of the proteins, can exhibit these same effects absent any biological context.⁹ These findings suggest that synthetic molecules might be discovered that can serve as accelerants of crystallization processes in industrial settings. Moreover, design of molecules that mimic the action of these natural biopolymers, but are much more stable against high pressures, temperatures and acidic conditions would result in a technology that is broadly applicable to industrial crystallization. Herein, we report that peptoids, a novel class of sequence-specific non-natural biomimetic polymers, can be designed and synthesized to mimic peptides and proteins for mineralization of CaCO₃. We identified a set of amphiphilic peptoids that significantly accelerate mineralization of CaCO₃ even under very low concentration (nM range). We expect this research will allow for rational design of peptoids as catalysts for geologic CO₂ sequestration, mimicking the living organisms based natural sequestration of CO₂.

Peptoids, or poly-N-substituted glycines, are a novel class of non-natural polymers developed to mimic both the structure and functionality of peptides and proteins, and bridge the gap between biopolymers and bulk polymers.¹⁰⁻¹² As with peptides, sequence-specific peptoids can be efficiently and cheaply synthesized by using automated solid-phase synthesis starting from a large number of chemically diverse amine building blocks.¹³ Moreover, peptoids exhibit much higher protease stability¹⁴ and structural stability¹⁵ than peptides or proteins. The interesting structural features and properties of peptoids prompted us to tackle the challenging issue of geologic CO₂ sequestration: development of catalysts which can possibly be used in geological reservoirs for efficient conversion of CO₂ to CaCO₃ minerals.⁶

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