



Ab initio study of thermodynamic, structural, and elastic properties of Mg-substituted crystalline calcite

Pavlına Elstnerová^{a,b}, Martin Friák^{a,*}, Helge Otto Fabritius^a, Liverios Lymperakis^a, Tilmann Hickel^a, Michal Petrov^a, Svetoslav Nikolov^c, Dierk Raabe^a, Andreas Ziegler^d, Sabine Hild^e, Jörg Neugebauer^a

^a Department of Computational Materials Design, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Strasse 1, Düsseldorf 40237, Germany

^b Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno 611 37, Czech Republic

^c Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 4, 1113 Sofia, Bulgaria

^d Central Facility for Electron Microscopy, University of Ulm, Albert-Einstein-Allee 11, Ulm 89069, Germany

^e Department of Polymer Science, Johannes Kepler University Linz, Altenbergerstrasse 69, Linz 4040, Austria

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ABSTRACT

Arthropoda, which represent nearly 80% of all known animal species, are protected by an exoskeleton formed by their cuticle. The cuticle represents a hierarchically structured multifunctional biocomposite based on chitin and proteins. Some groups, such as Crustacea, reinforce the load-bearing parts of their cuticle with calcite. As the calcite sometimes contains Mg it was speculated that Mg may have a stiffening impact on the mechanical properties of the cuticle (Becker et al., Dalton Trans. (2005) 1814). Motivated by these facts, we present a theoretical parameter-free quantum-mechanical study of the phase stability and structural and elastic properties of Mg-substituted calcite crystals. The Mg-substitutions were chosen as examples of states that occur in complex chemical environments typical for biological systems in which calcite crystals contain impurities, the role of which is still the topic of debate. Density functional theory calculations of bulk $(\text{Ca,Mg})\text{CO}_3$ were performed employing 30-atom supercells within the generalized gradient approximation as implemented in the Vienna Ab-initio Simulation Package. Based on the calculated thermodynamic results, low concentrations of Mg atoms are predicted to be stable in calcite crystals in agreement with experimental findings. Examining the structural characteristics, Mg additions nearly linearly reduce the volume of substituted crystals. The predicted elastic bulk modulus results reveal that the Mg substitution nearly linearly stiffens the calcite crystals. Due to the quite large size-mismatch of Mg and Ca atoms, Mg substitution results in local distortions such as off-planar tilting of the CO_3^{2-} group.

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In the course of evolution nature has developed numerous materials with outstanding functional and structural properties. These structures mostly consist of an organic matrix of structural biopolymers which is modified and reinforced with various proteins and biominerals [1–9]. Such materials possess excellent stiffness, toughness, and strength related to their low density, while the mechanical characteristics of their underlying constituents are rather modest [8,10]. This remarkable performance is a consequence of their hierarchical structure, the specific design at each level of organization and the inherent strong heterogeneity [10]. Therefore, to understand macroscopic mechanical properties of these materials, one should take into account their structure–property relations at all length scales down to the molecular level. Hence, multiscale modeling that can systematically describe and investigate material properties from the atomistic scale up to the

macroscopic level has become the most widely used method for tackling the structure–property relations of biological nanocomposites and has been applied to bone, nacre, mother of pearl, arthropod cuticle, and other materials (e.g. [7,11–16]).

Recently Nikolov et al. [17,16] developed a bottom-up multiscale approach to model hierarchically structured nanocomposites. This approach combines quantum mechanical *ab initio* calculations with hierarchical homogenization continuum methods and has been successfully applied to study the elastic properties of the chitin-based mineralized cuticle of an arthropod, the lobster *Homarus americanus*. In this hierarchical constitutive model *ab initio* calculations are used to describe the ground-state structure and elastic properties of chitin which are relevant on the nanometer-scale where experimental data are missing. However, the properties of these materials do not depend only on the specific microstructure at all levels of hierarchy but also on the chemical composition of both the organic and inorganic components. Among the over 60 different biogenic minerals known at

* Corresponding author. Tel.: +49 211 67 92 461.

E-mail address: friak@mpie.de (M. Friák).

present [1–4,6], Ca carbonate is the most widespread biomineral used by invertebrates. It serves as the skeletal element in the shells of marine protists and corals, as material for the shells of molluscs and echinoderms, and in the exoskeletons of crustaceans [18]. In these organisms, it occurs either in its amorphous form (ACC) or as crystalline calcite, which is frequently associated with significant amounts of Mg. In crustaceans, the presence of Mg calcite has been shown for a number of species [19,20], and an Mg content as high as 11% was reported in biogenic calcite samples taken from the spines and the body skeleton of the sea urchin *Paracentrotus lividus* [21]. It was speculated [22] that the Mg content may affect the mechanical properties of the cuticle since Mg calcite is harder than calcite without Mg, suggesting that it is formed for mechanical reasons. Fig. 1a shows an electron micrograph of a microtome polished cross-section from the dorsal carapace of a large decapod crustacean, the edible crab *Cancer pagurus* and its elemental composition measured by energy dispersive X-ray spectrometry (EDX), showing the presence of Ca, O, C, P, Ca and Mg. Qualitative EDX mappings show the heterogeneous distribution of Ca (Fig. 1b), Mg (Fig. 1c) and P (Fig. 1d) in the two mechanically relevant main layers, the exocuticle and endocuticle. Similar inhomogeneous distributions of organic and inorganic components within crustacean cuticles have been reported earlier [23,24], and were correlated to the functions of particular skeletal

elements. Ca carbonate plays a generally important role in the structure and mechanic properties of these materials. However, there is still an ongoing debate about the specific role of Mg. In addition to enhancing the mechanical properties of calcite, it has also been proposed that Mg^{2+} ions can block the formation of calcite in the presence of biopolymers and therefore favour precipitation of amorphous $CaCO_3$ [25]. Studying the thermodynamic, structural, and elastic properties of Mg-substituted crystalline calcite on the molecular level can help to gain a deeper understanding of the role Mg plays in biological materials.

Previous theoretical calculations, based on valence force field as well as *ab initio* methods, on the system of Ca and Mg carbonates have focused on the thermodynamics, structural, vibrational and elastic properties for the stoichiometric end-members of the pseudobinary alloy system $Ca_nMg_m(CO_3)_{n+m}$ [26–35]. The energetics and atomic geometry of Mg-substitutions in calcite have been addressed by using Hartree–Fock linear-combination-of-atomic-orbitals (HF-LCAO) calculations [36]. However, a detailed study on the atomic geometry, the energetics, and the elastic properties of the pseudobinary alloy system $Ca_nMg_m(CO_3)_{n+m}$ for the whole range of compositions is lacking. Therefore, in the present study we focus on the mineral matrix inhomogeneities and address the elastic properties of calcite ($CaCO_3$), magnesite ($MgCO_3$) and the pseudobinary alloy system $Ca_nMg_m(CO_3)_{n+m}$.

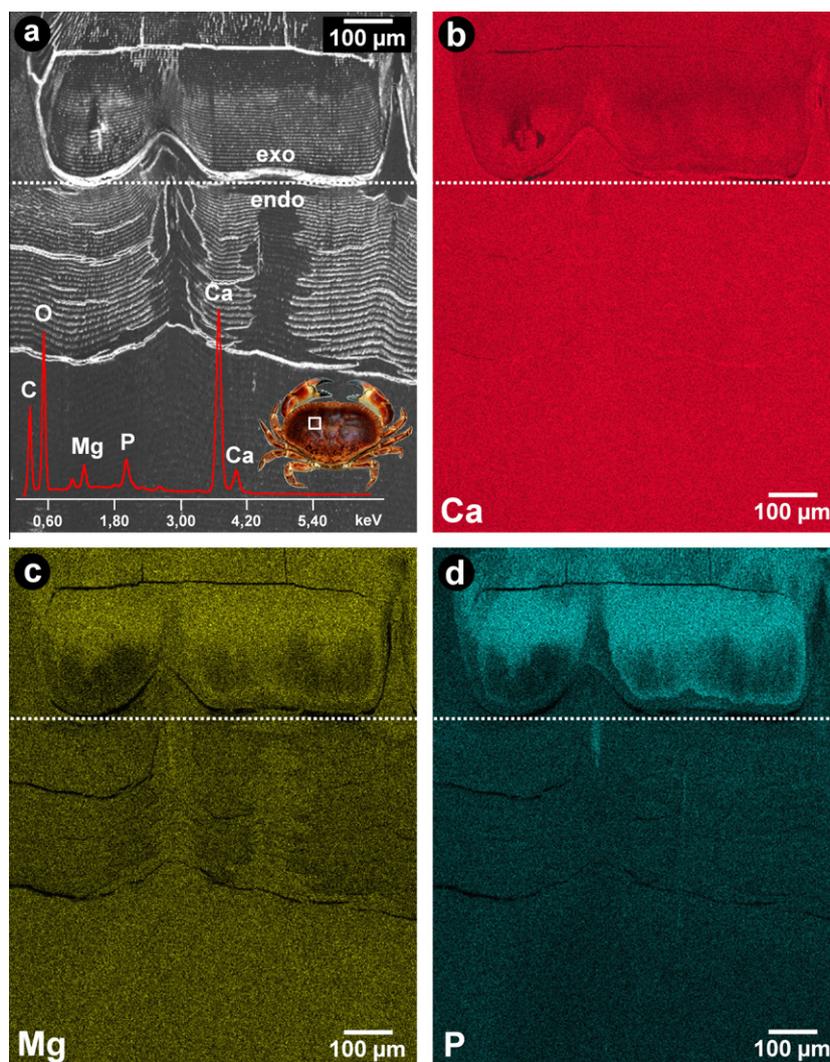


Fig. 1. Elemental distribution in cuticle from the dorsal carapace of the crab *Cancer pagurus*. (a) Electron micrograph of a microtome-polished cross-section showing the two structurally different main layers exocuticle (exo) and endocuticle (endo) and the elemental composition measured by qualitative energy dispersive X-ray spectrometry (EDX). (b–d) Qualitative EDX mapping showing the heterogeneous distribution of Ca (b), Mg (c) and P (d) throughout the thickness of the cuticle.

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