Understanding the Interactions Between Small Molecule Adsorbates and Calcium-Terminated Aragonite Surfaces: A Density Functional Theory Approach

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Introduction

- Aragonite is a high pressure polymorph of calcium carbonate ($CaCO_3$)
  - Metastable under conditions at the surface of the Earth
  - Orthorhombic crystal structure
  - Converts to calcite, a more stable polymorph of $CaCO_3$, on a timescale of 10^7 - 10^8 years
  - Found in the ocean (coral, mollusk shells) and caves (stalactites, natural deposits of minerals)

Left: Calcite (left) and aragonite (right) crystals. Image © MIT News
Right: Cartouche-shaped snuff box, Mother-of-pearl, The Walters Art Museum

- Relevance to art conservation and art conservation science: Found in mother-of-pearl, shells, sculptural material (limestone, marble), and historical pigments and paints
- Concerns of accelerated degradation by acidic adsorbates
  - Must consider increased sanitization inside museums, which could result in an increase in the concentration of potentially harmful molecules in the atmosphere
- DFT data will allow conservators to predict how selected adsorbates interact with aragonite and guide treatment, storage, and display protocols
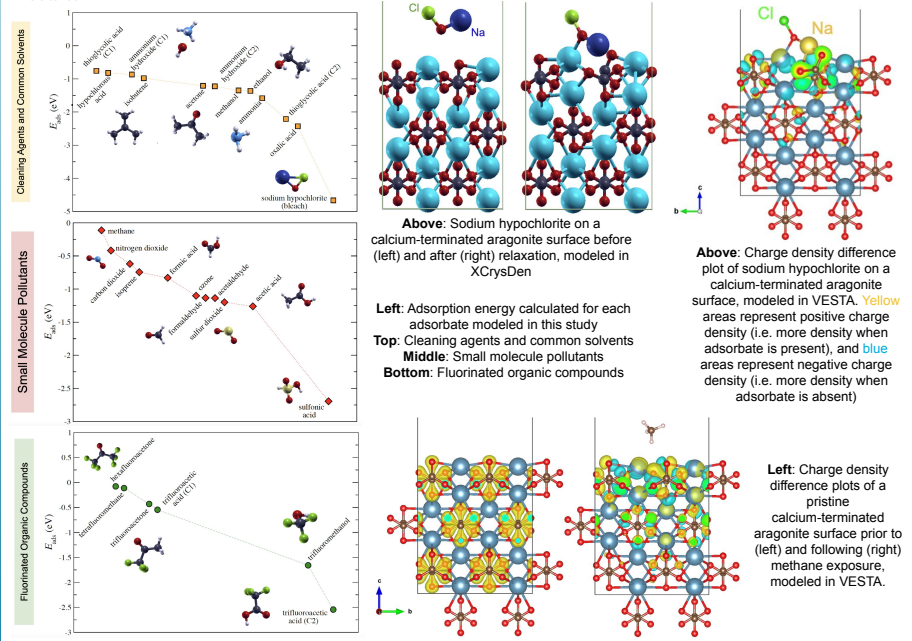
Project Goals

To use computational chemistry as a tool to model the interactions between potential pollutants and cleaning agents and aragonite, a mineral surface relevant to art conservation and art conservation science.

Methodology

All calculations described here employ periodic DFT methods (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) and are carried out using Quantum Espresso, an open source software package (Giannozzi et al., 2009; Giannozzi et al., 2017). All atoms are represented using GBRV-type ultrasoft pseudopotentials (Vanderbilt, 1990; Garrity et al., 2014). A plane-wave cutoff of 40 Ry and charge density cutoff of 320 Ry are employed for all calculations, in line with similar surface studies (Bennett, Jones, Hamers, et al., 2018; Bennett, Jones, Huang, et al., 2018; Bennett et al., 2020). Bulk structural relaxations use a 6x6x6 k-point grid (Monkhorst and Pack, 1976), and the convergence criteria for self-consistent relaxations is 5x10⁻⁶ eV. Geometry optimization of all surface-adsorbate interactions did not include fixing any layers, as detailed in Corum et al. (2017) where all atoms are free to relax. All calculations are performed at the GGA level using the Wu-Cohen (WC) modified PBE-GGA exchange correlation functional for solids (Perdew et al., 1996; Wu and Cohen, 2006).

Results

Cleaning Agents and Common Solvents

Small Molecule Pollutants

Fluorinated Organic Compounds

Above: Sodium hypochlorite on a calcium-terminated aragonite surface before (left) and after (right) relaxation, modeled in XCrysDen

Left: Adsorption energy calculated for each adsorbate modeled in this study
Top: Cleaning agents and common solvents
Middle: Small molecule pollutants
Bottom: Fluorinated organic compounds

Above: Charge density difference plot of sodium hypochlorite on a calcium-terminated aragonite surface, modeled in VESTA. Yellow areas represent positive charge density (i.e. more density when adsorbate is present), and blue areas represent negative charge density (i.e. more density when adsorbate is absent)

Left: Charge density difference plots of a pristine calcium-terminated aragonite surface prior to (left) and following (right) methane exposure, modeled in VESTA.

Conclusions

- DFT was used to analyze the interactions of cleaning agents, solvents, and pollutants on a calcium-terminated aragonite surface
- Cleaning agents/common solvents interact more with the aragonite surface than small molecule pollutants; however, the use of cleaning agents can be more easily controlled by conservators
- Electronegative functional groups (e.g. carboxylic acid) tend to be highly reactive with the metal-terminated surface
- Strongest to weakest interactions: polar protic > polar aprotic > nonpolar adsorbates
- Conservators should be careful even when using recommended cleaners for aragonite such as oxalic or thioglycolic acid
- Museums must also consider the long-term effects of using common disinfectants such as bleach or ethanol

Jar with Cartouches of Merneptah, Egypt, ca. 1213-1203 BC, Aragonite, The Metropolitan Museum of Art

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