Utilizing Density Functional Theory to Model Small Molecule-Aragonite Interactions Relevant to Cultural Heritage

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Introduction

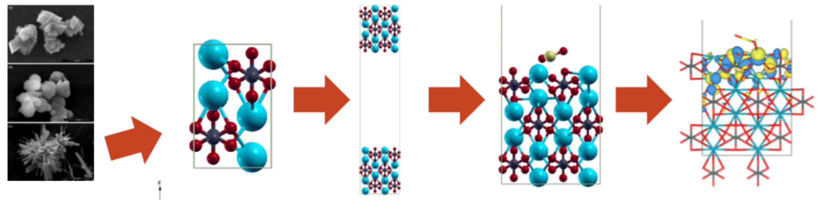
- Aragonite is a high-pressure polymorph of $CaCO_3$ commonly found in oceans, caves, and in the shells/skeletons of marine animals.
- Aragonite is relevant to cultural heritage, especially for cultures near the ocean. It is a component in historical pigments and paints and the shells of mollusks. Historical material like sculptures may also have aragonite as its main component.
- When exposed to certain conditions, it can easily degrade.
- DFT is a quantum mechanical method of calculating the electron density of atoms, molecules, and surfaces. It uses the reductionist approach gain information through simplifying the problem.

A) Sultepec. *Mask*. 600-300 BC (Late Formative), Aragonite, The Walters Art Museum, Baltimore.
B) *Jar with Cartouches of Merneptah*. 1213-1203 BC, Aragonite, The Metropolitan Museum of Art,New York
C) *Cylinder Seal*. 2400 BC-2200 BC, Aragonite, The British Museum, London.

Project Goals

1. Examine and model different functional group interactions using DFT
2. Create damage mitigation procedures based on data trends
3. Predict how complicating environmental factors may compound present damage
4. Assess different conservation approaches to address resulting problems

Methods



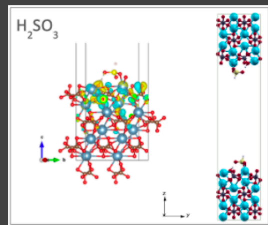
Computational Details

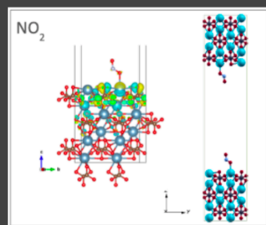
All calculations described here employ periodic DFT methods (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) and are carried out using Quantum Espresso, an open-source software package (Giannozzi et al., 2009; Giannozzi et al., 2017). All atoms are represented using GBRV-type ultrasoft pseudopotentials (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

C Center	O & N Center	S Center

	Adsorbate	Ea (eV)	Protonated Surface
2p	NO_2	-0.42	0.18
	CO_2	-0.62	-0.27
	HCOOH	-0.83	
	O_3	-1.10	-0.09
	CH_2O	-1.14	
3p	SO_2	-1.20	-0.64
	H_2S	-1.20	
2p	H_2O	-2.05	
	CH_3COOH	-2.50	
3p	SO_3	-3.34	
	SO_4H_2	-3.47	
	SO_3H_2	-3.64	





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Conclusions

- The adsorbates SO_3, $H2SO_4$, and $H2SO_3$ have the strongest interactions, while NO_2 and CO_2 have the weakest. SO_2 and H_2S had weaker interactions than the other sulfur-centered adsorbates due to the S oxidation state.
- A conservation recommendation: Prioritize removing sulfur-containing adsorbates when displaying aragonite-containing artifacts.
- Conclusion: pKA is not a sufficient guide to predict interactions.
- While exploring protonated surface trends, future works can focus on finding effective filtration for the 3p sulfur-containing molecules and analyzing current display case absorbers' effectiveness and interactions with aragonite surfaces. Filters such as activated charcoal, potassium permanganate, and silica gel have been shown to help remove one or more of the following pollutants: ozone, formaldehyde, nitrogen dioxide, sulfur dioxide and hydrogen sulfide.
- Future projects can also investigate the uses of aragonite in restoration instead of the conservation of aragonite surfaces. The findings can be expanded and applied to aragonite's uses as the agent for removing pollutants from other surfaces like bronze statues.

References

Hohenberg, P., *Kohn, W.,* 1964. Inhomogeneous electron gas. Phys. Rev. 136 (3B), B864-B871.

Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. Phys. Rev. 140 (4A), A1133-A1138.

Giannozzi, P., *et al,* 2017. Advanced capabilities for materials modelling with Quantum ESPRESSO. J. Phys.-Condens. Mat. 29 (46), 465901.

Giannozzi, P., *et al*., 2009. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys.-Condens. Mat. 21 (39), 395502.

Vanderbilt, D., 1990. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys. Rev. B 41 (11), 7892-7895.

Garrity, K.F., Bennett, J.W., Rabe, K.M., Vanderbilt, D., 2014. Pseudopotentials for high-throughput DFT calculations. Comp. Mater. Sci. 81, 446-452.

Bennett, J.W., Jones, D.T., Hamers, R.J., Mason, S.E., 2018. First-principles and thermodynamics study of compositionally tuned complex metal oxides: Cation release from the (001) surface of Mn-rich lithium nickel manganese cobalt oxide. Inorg. Chem. 57 (21), 13300-13311.

Bennett, J.W., Jones, D., Huang, X., Hamers, R.J., Mason, S.E., 2018. Dissolution of complex metal oxides from first-principles and thermodynamics: Cation removal from the (001) Surface of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$. Environ. Sci. Technol. 52 (10), 5792-5802.

Bennett, J.W., *et al*, 2020. Emerging investigator series: first-principles and thermodynamics comparison of compositionally-tuned delafossites: cation release from the (001) surface of complex metal oxides.

Monkhorst, H.J., Pack, J.D., 1976. Special points for Brillouin-zone integrations. Phys. Rev. B 13 (12), 5188-5192.

Corum, K.W., Huang, X., Bennett, J.W., Mason, S.E., 2017. Systematic density functional theory study of the structural and electronic properties of constrained and fully relaxed (0 0 1) surfaces of alumina and hematite. Mol. Simulat. 43 (5-6), 406-419.

Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. Phys. Rev. Lett. 77 (18), 3865-3868.

Wu, Z., Cohen, R.E., 2006. More accurate generalized gradient approximation for solids. Phys. Rev. B 73 (23), 235116.