The Impact of Nitrates and Phosphates on the Surface of Calcite: A First-Principles Analysis of Calcium Carbonate

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INTRODUCTION

- Calcite is a major component of limestone, a material commonly used in sculpture.[1]
- Salt adsorbates have been found to be corrosive to limestone.[2]
- Here we compare phosphate (-3 charge) and nitrate (-1 charge) anions as surface salts.

Bearded Man, Walters Art Museum

METHODOLOGY

All calculations described here employ periodic DFT methods[3,4] and are carried out using Quantum Espresso, an open source software package[5,6]. All atoms are represented using the GBRV-type ultrasoft pseudopotentials[7,8]. 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[9-11]. Bulk structural relaxations use a 6x6x6 k-point grid[12]. Geometry optimization of all surface-adsorbate interactions did not include fixing any layers, as detailed in Corum *et al.*[13] where all atoms are free to relax. All calculations are performed using the Wu-Cohen (WC) modified PBE-GGA exchange correlation functional for solids[14-15].

ACKNOWLEDGEMENTS

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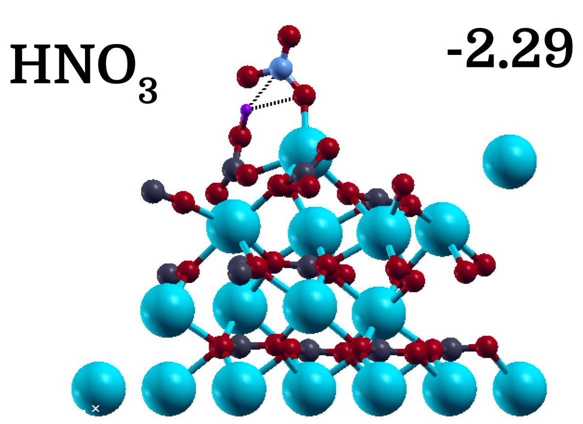
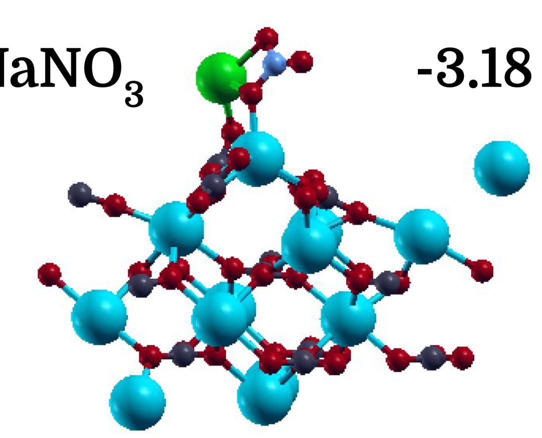
PROJECT GOALS

- Understand interactions between various nitrate and phosphate salts on two differently terminated calcite surfaces
- Elucidate trends in adsorption energy (E_{ads}) to determine how difficult salt removal would be in desalination efforts[16]

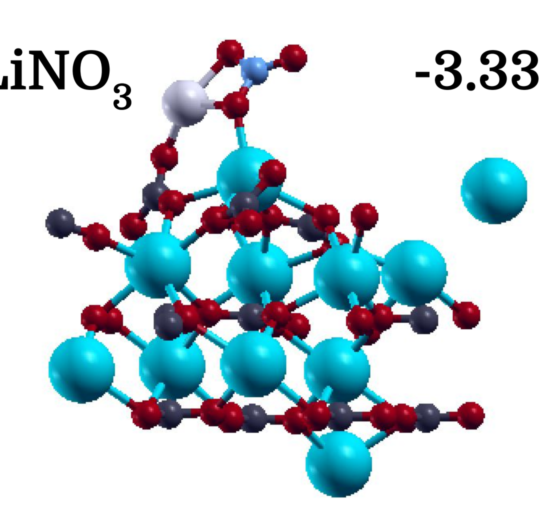
HNO_3 -2.29 eV



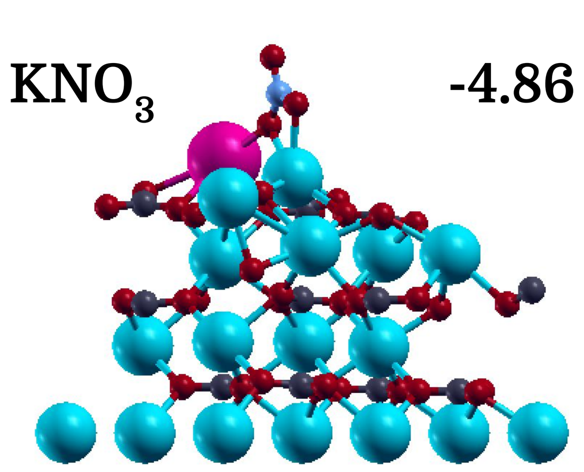
$NaNO_3$ -3.18 eV

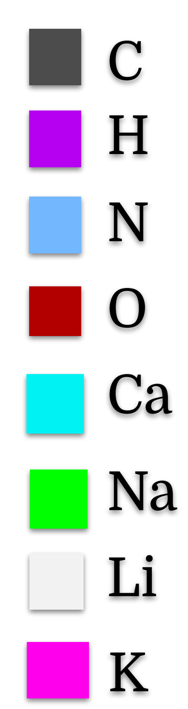


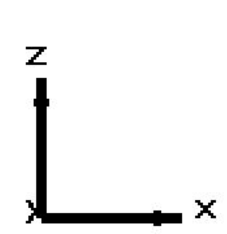
$LiNO_3$ -3.33 eV



KNO_3 -4.86 eV





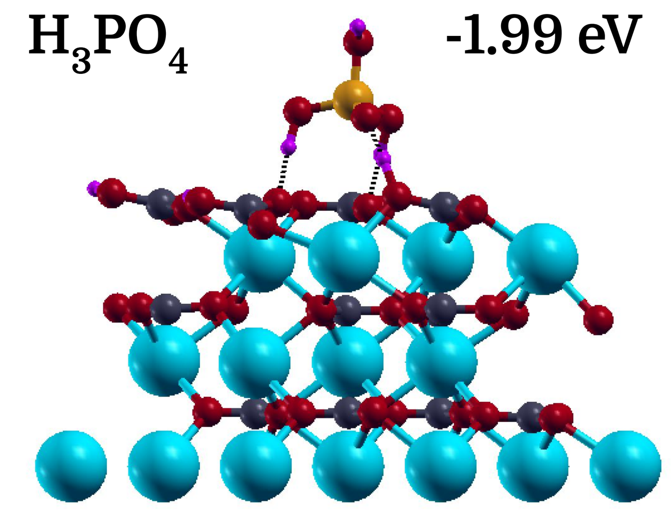


RESULTS

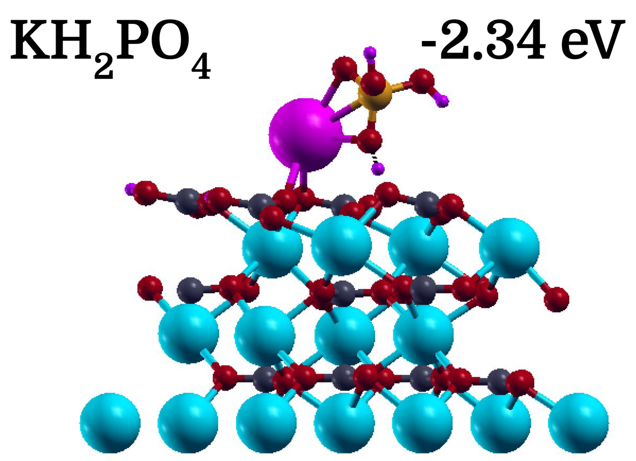
Table 1. Adsorption Energies (E_{ads}) on Ca- and H-Terminated Surfaces

Adsorbate	E_{ads} (eV) Ca-Term	E_{ads} (eV) H-Term
$Mg_3(PO_4)_2$	-12.14	-13.62
$Ca_3(PO_4)_2$	-11.33	-10.38
K_3PO_4	-8.99	-5.51
$Mg_2H_2(PO_4)_2$	-8.19	-6.22
Na_3PO_4	-6.74	-5.37
Na_2HPO4	-6.66	-5.32
K_2HPO_4	-5.69	-4.82
NaH_2PO4	-5.13	-4.05
Li_3PO_4	-4.89	-1.91
KNO_3	-4.86	-1.82
KH_2PO_4	-4.55	-2.34
$LiNO_3$	-3.33	-1.91
$NaNO_3$	-3.18	-2.58
H_3PO_4	-3.17	-1.99
$Mg(NO_3)_2$	-3.17	-0.08
$Ca(NO_3)_2$	-3.06	-0.17
HNO_3	-2.29	-0.96
NH_4NO_3	-2.20	-

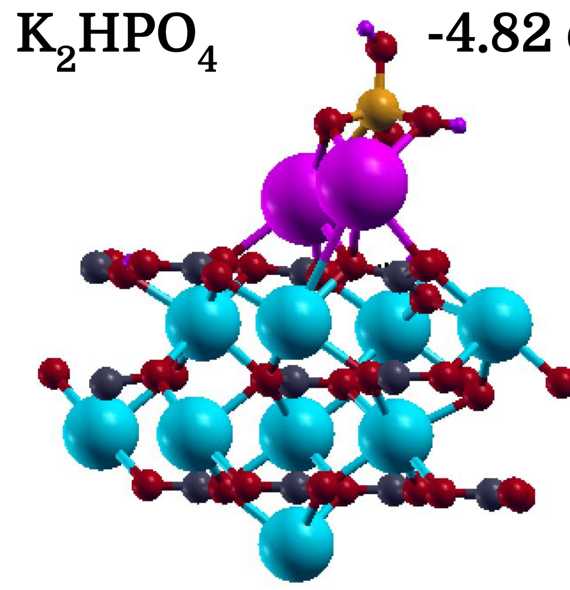
H_3PO_4 -1.99 eV



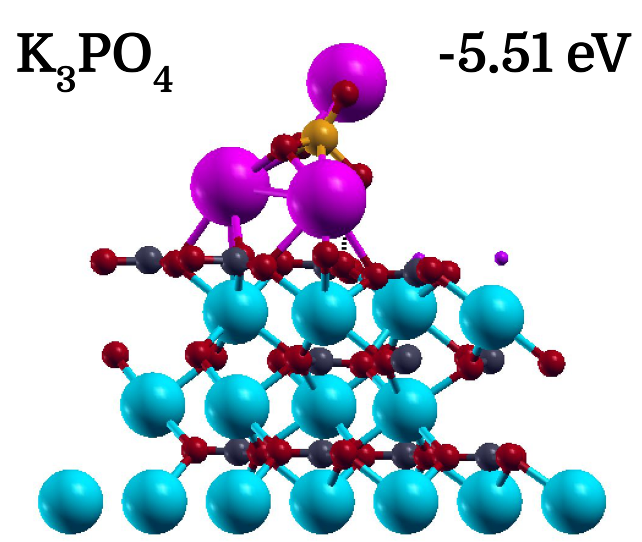
KH_2PO_4 -2.34 eV



K_2HPO_4 -4.82 eV



K_3PO_4 -5.51 eV



The nitrate series (**left**) is shown on the calcium terminated surface. The phosphate series (**above**) is shown on the proton terminated surface.

CONCLUSIONS

- Phosphate salts had more negative E_{ads} on both the calcium and proton terminated calcite surfaces when compared to nitrate salts.
- Overall, the adsorbates interacted more strongly with the calcium-terminated surface than with the proton-terminated surface.
- Metal cations were found to adsorb readily to calcite when compared to anion adsorbates with a higher proton count.
- As you replace cations with elements that increase in atomic radius, the adsorption energy gets increasingly more negative.
- Cations that are most similar to calcium in size and charge integrate best into the surface and have more favorable adsorption energies.

REFERENCES

1) Gettens, R. J. *et al. Stud. Conserv.* **1974**, 19 (3), 157.
2) Charola, A. E. *et al. RBM* **2001**, 7 (2).
3) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, 136 (3B), B864–B871.
4) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, 140 (4A), A1133–A1138.
5) Giannozzi, P. *et al. J. Condens. Matter Phys.* **2017**, 29 (46), 465901.
6) Giannozzi, P. *et al. J. Condens. Matter Phys.* **2009**, 21 (39), 395502.
7) Vanderbilt, D. *Phys. Rev. B* **1990**, 41 (11), 7892–7895.
8) Garrity, K. F. *et al. Comput. Mater. Sci.* **2014**, 81, 446–452.
9) Bennett, J. W. *et al. Inorg. Chem.* **2018**, 57 (21), 13300–13311.
10) Bennett, J. W. *et al. Environ. Sci. Technol.* **2018** 52 (10), 5792–5802.
11) Bennett, J. W. *et al. Environ. Sci. Nano* **2020**, 7 (6), 1642–1651.
12) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, 13 (12), 5188–5192.
13) Corum, K. W. *et al. Mol. Simulat.* **2017**, 43 (5-6), 406–419.
14) Perdew, J. P. *et al. Phys. Rev. Lett.* **1996**, 77 (18), 3865–3868.
15) Wu, Z.; Cohen, R. E. *Phys. Rev. B* **2006**, 73 (23).
16) Abel, J. B. *et al.* Preprint from the Michael C. Carlos Museum at Emory University.
17) A. Kokalj, J. *Comput. Mater. Sci.* **2003**, 28 (2), 155-168.