

## Effects of phosphate ions on aragonite and calcite in aqueous environments

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We show that the presence of inorganic phosphate ( $\text{PO}_4^{3-}$ ) in aqueous suspensions of  $\text{CaCO}_3$  causes two effects with interesting geochemical applications. First,  $\text{PO}_4^{3-}$  induces consistently different zeta (surface) potentials between calcite and aragonite under many, but not all, aqueous suspension preparation conditions. Thus,  $\text{PO}_4^{3-}$ -altered zeta potentials could be an effective proxy for assessing surface chemistry differences among some naturally occurring forms of  $\text{CaCO}_3$ . Second, we show that short term exposure to mM levels of  $\text{PO}_4^{3-}$  stabilizes aragonite against aqueous dissolution for many months. Furthermore, the stabilized aragonite shows no distinct phosphate-containing mineral surface phases. This has potential implications for aragonite persistence in wet environments. These findings come from studying the effect of mM level of different inorganic  $\text{PO}_4^{3-}$  sources on the zeta potentials of a variety of hand-ground calcite and aragonite powders, both naturally occurring and laboratory-produced, in aqueous suspensions. Our findings expose several critical knowledge gaps related to polymorph-specific carbonate surface chemistry, which are directly relevant for understanding and predicting the reactivity of  $\text{CaCO}_3$  in geological contexts. It is widely known that  $\text{CaCO}_3$  particles do not yield stable suspensions in pure water, because these particles have small surface charges and thus tend to coagulate [1]. It is also widely known that low concentrations of  $\text{PO}_4^{3-}$  will drastically increase the level of negative surface charge and stabilize such a suspension [2]. However, there are relatively few investigations that attempt to address the surface interactions between phosphate ions and different  $\text{CaCO}_3$  polymorphs [3,4,5]. Our studies offer incentives for additional investigations in this area by providing zeta potential data that is correlated with time-dependent studies of suspension pH, and Fourier transform infrared spectra.

[1] Moulin, Roques (2003) *J. Colloid Interface Sci.* **261**, 115-126. [2] Tian, Yang, Zhu, Liu, Li (2015) *J. Phys. Chem. C* **119**, 4856-4864. [3] Millero, Huang, Zhu, Liu, Zhang (2001) *Aquatic Geochem.* **7**, 33-56. [4] Kababya, Gal, Kahil, Weiner, Addadi, Schmidt (2015) *J. Am Chem. Soc.* **37**, 990-998. [5] Xu, Chen, Zhou, Wang, Yin, Chen (2014) *RSC Adv.* **4**, 35205-35214.