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Large Effect of Hydration on ^{18}O Fractionation between H_2O and CO_3^{2-}: Implications for the pH-carbonate-δ^{18}O Relationship and Inferred Climate Changes

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Stable oxygen isotope fractionation in the system H_2O-CO_3^{2-}-HCO_3^--CO_2-$CaCO_3$ is fundamental both to geochemical proxy applications such as paleothermometry and as a set of physico-chemical constants. Moreover, the pH effect on carbonate-δ^{18}O plays a crucial role in a current controversy on the primary driver of Phanerozoic climate change (Shaviv and Veizer, 2003; Rahmstorf et al., 2004). Yet our understanding of the system's isotope basics is still limited. For example, the effect of hydration on the ^{18}O fractionation between H_2O and ionic species such as CO_3^{2-} (α_{cw}) is hitherto unknown and inaccessible to experimental means. Classical theory assumes molecules in the gas phase and predicts unrealistic α_{cw}. I have calculated the coordination of water molecules within the CO_3^{2-} hydration sphere using *ab initio* molecular orbital theory. I will propose possible structures of the $CO_3^{2-}(H_2O)_n$ cluster. The results show that the effect of hydration on α_{cw} may be as large as 10 per mil (^{18}O enrichment), compared to a 'gas phase-ion'. My new results for α_{cw} are in agreement with recent independent experimental and theoretical efforts. These findings have important consequences for the pH effect on the carbonate-δ^{18}O proxy and for our understanding of vital effects in biogenic carbonates. Relations to δ^{18}O-paleothermometry and past climate changes that have been proposed elsewhere will be discussed.