

Molecular Paleoclimatology: Quantum Chemistry and the History of the Earth's Atmosphere

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The history of the composition of the Earth's atmosphere is one of the most important problems of our time. As the human race considers the possibility of planetary engineering to mitigate the potential effects of CO₂-induced global warming, clearer insight into the history of atmospheric PCO₂ and global temperature is required. For example, if PCO₂ values were 20 times higher at times in the geologic past, it may be premature to worry about anthropogenic increases in PCO₂ a factor of two above Pleistocene-Holocene values, which are anomalously low from the point of view of geologic history. Two major techniques for determining the history of atmospheric PCO₂ are the chemically based. The first depends on the isotopic composition of carbon incorporated into soil minerals during their growth. The second depends on the isotopic composition of boron incorporated into marine minerals during precipitation. Both methods depend crucially on knowing the equilibrium constant for isotope exchange between minerals, aqueous, and gas phases. There are major uncertainties in these equilibrium constants which strongly affect geochemical estimation of the history of PCO₂ in Earth's atmosphere. Here, I describe how quantum chemistry techniques can be used to reduce this uncertainty and make more reliable estimates of PCO₂ values. Ab initio molecular dynamics and quantum chemistry techniques are used to calculate the structure, vibrational frequencies, and carbon-isotope fractionation factors of the carbon dioxide component [CO₂(m)] of soil (oxy)hydroxide minerals goethite, diaspore, and gibbsite. We have identified two possible pathways of incorporation of CO₂(m) into (oxy)hydroxide crystal structures: one in which the C⁴⁺ substitutes for four H⁺ [CO₂(m)_A] and another in which C⁴⁺ substitutes for (Al³⁺, Fe³⁺) + H⁺ [CO₂(m)_B].

Calculations of isotope fractionation factors give large differences between the two structures, with the CO₂(m)_A being isotopically lighter than CO₂(m)_B by 10 per mil in the case of gibbsite and nearly 20 per mil in the case of goethite. The reduced partition function ratio of CO₂(m)_B structure in goethite differs from CO₂(g) by <1 per mil. The predicted fractionation for gibbsite is >10 per mil higher, close to those measured for calcite and aragonite. The surprisingly large difference in the carbon-isotope fractionation factor between the CO₂(m)_A and CO₂(m)_B structures within a given mineral suggests that the isotopic signatures of soil (oxy) hydroxide could be heterogeneous.

Density functional and correlated molecular orbital calculations (MP2) are carried out on B(OH)₃·nH₂O clusters (n = 0, 6, 32) and B(OH)₄nH₂O (n = 0, 8, 11, 32) to estimate the equilibrium distribution of ¹⁰B and ¹¹B isotopes between boric acid and borate in aqueous solution. For the large 32-water clusters, multiple conformations are generated from ab initio molecular dynamics simulations to account for the effect of solvent fluctuations on the isotopic fractionation. We provide an extrapolated value of the equilibrium constant $\ln K$ for the isotope exchange reaction $10\text{B(OH)}_3(\text{aq}) + 11\text{B(OH)}_4(\text{aq}) = 11\text{B(OH)}_3(\text{aq}) + 10\text{B(OH)}_4(\text{aq})$ of 1.026—1.028 near the MP2 complete basis set limit with 32 explicit waters of solvation. With some exchange-correlation functionals we find potentially important contributions from a tetrahedral neutral B(OH)₃·H₂O Lewis acid–base complex. The extrapolations presented here suggest that DFT calculations give a value for $\ln K$ about 15 % higher than the MP2 calculations.