Ab initio study of oxygen isotope fractionation during CO_2 production from calcium carbonate and phosphoric acid reaction

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Isotope ratios in different carbonate minerals are the key to the past Earth surface temperature, pH etc. In isotope geochemistry laboratories carbonate after reaction with phosphoric acid yield carbon dioxide which is analyzed for oxygen isotope ratios. This is the most useful tool for palaeo temperature reconstruction [1,2]. To the best of our knowledge, the only work (Guo et al.[3]) provided a theoretical basis to relate oxygen isotope ratios derived from CO_2 after reacting carbonates with reaction temperature. We propose a mechanism in which we use kinetic isotope fractionation and transition state theory involving both the reactants (unlike Guo et al.[3] where only one reactant was used with one product to form the transition state and there was no phosphoric acid molecule in the cluster model) and show how the reaction proceeds and which oxygen isotope is contributing to the product CO_2. We use the surface structure of $CaCO_3$ crystal which is a dimer[4]. Ab-initio density function theory is used to calculate the transition states and energies of the reactions. We also show the potential energy surface on which the reaction proceeds and CO_2 produces. For different isotopic molecules of the calcium carbonate as the electronic property is same, the potential energy surface remains the same changing the vibrational energy due to mass difference and that account for the change in rate of the chemical reactions in case of different isotopologues. For all our calculations Gaussian09 package [5] is used. Here we will discuss the role of acid reaction temperature on the oxygen isotope ratios in product CO_2.

[1] Ghosh et al., *Geochimica et Cosmochimica Acta 71 (2007) 2736–2744*. [2] Dennis et al., *Geochimica et Cosmochimica Acta 75 (2011) 7117–7131*. [3] Weifu Guo et al., *Geochimica et Cosmochimica Acta 73 (2009) 7203–7225*. [4] Mao and Siders, *Journal of Molecular Structure (Theochem) 419 (1997) 173–184*. [5] M. J. Frisch et al. Gaussian 09, Revision A.02