The role of electronic structure in water exchange reactions

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The focus of this study is on the kinetics of the interfacial exchange reaction of water with different metal oxides. Specifically we have chosen to study two metal oxide complexes $M_3O_2(H_2O)_3(CH_3CO_2)_6^{+2}$ where M=Mo and W, because of the unique kinetics of these two complexes. Despite having an identical geometry, and the same rate of water exchange, one complex has a negative activation volume (W) and the other positive (Mo). This indicates that the two complexes could have two completely different mechanisms for exchange. According to Swaddle's semi-empirical model a negative activation volume is an associative-interchange activation state while a positive volume is a dissociative-interchange state. The other possibility is that differences in polarisation of the metal oxygen bonds leads to changes in the entropy of activation, which correlates to a volume change. We used DFT to elucidate the reaction pathways for both species and determine the exchange kinetics and thermodynamics. This study is of particular importance to geochemists because Tungsten is known to have anomalous exchange reaction behavior and insights into this cluster should provide insights for Tungsten mineral surface reactions. While both metals are only trace constituents of most geochemical systems, both are of increasing interest due to their biological effects and their use in electronic and metalurgical applications.

Can $\delta^{13}C_{phyto}$ be used to discern the change of phytoplankton community: A case study in the impounded Wujiang River

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Carbon fractionation by phytoplankton is of species-specific characteristics [1], which provides the base on the potential possibility to discern the change of phytoplankton community. All factors that may affect the carbon isotopic compositions of phytoplankton could be reduced into two aspects. One is biological factors (e.g. the type of carboxylating enzyme). The other is environmental factors (e.g. light availability). The average values of $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$ and $\delta^{13}C_{phyto}$ were –8.2 ± 1.3‰ (n = 91, a range from –3.3 to –10.0‰), –29.5 ± 2.7‰ (n = 90, a range from –19.6 to –34.5‰), and –30.7 ± 4.3‰ (n = 78, a range from –15.1 to –39.2‰), respectively, in the investigated reservoirs. Seasonal fluctuation of $\delta^{13}C_{phyto}$ was comparable to that of $\delta^{13}C_{POC}$ and larger than that of $\delta^{13}C_{DIC}$. The $\delta^{13}C_{phyto}$ value showed a significant difference in different reservoirs. The value of $\delta^{13}C_{phyto}$ presented a significant correlation to that of $\delta^{13}C_{POC}$ (r=0.769, P<0.01, n=77), indicating that endogenetic phytoplankton is the main source of POC. Generally, diatom and green algae were the dominant algae in the investigated reservoirs. Blue algae were only found in eutrophic reservoirs in Oct. 2007. As a result, the variation of the contribution of diatom to the total phytoplankton (CDTP) can be an index to the changes in phytoplankton community. In this study, CDTP showed a significant negative correlation with $\delta^{13}C_{phyto}$ (r=-0.649, P<0.01, n=77) and ε ($\delta^{13}C_{phyto}$-$\delta^{13}C_{DIC}$; r=-0.648, P<0.01, n=77), suggesting that $\delta^{13}C_{phyto}$ can be used to discern the change of phytoplankton community in the impounded Wujiang River. Our study demonstrates that algal carbon fractionation is mainly controlled by algal species when environment factors affecting algal carbon isotope is hardly variable and/or the extent of their influences are far less than that of biological factors in a given field.

[1] Aberle & Malzahn (2007) *Oecologia* **154**, 291–303.