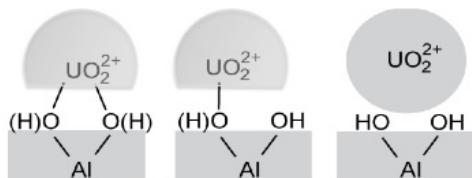


## Understanding Uranyl adsorption at the water-mineral interface: A theoretical approach

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In order to understand the physico-chemical properties of actinide complexes in the natural environment, we performed *ab initio* molecular dynamics (AIMD) simulations of the dynamic adsorption processes of uranyl at the water-mineral interfaces. Hydroxylated  $\alpha$ - $\text{Al}_2\text{O}_3$  surface is an important model system analogues for commonly occurring soil phase such as gibbsite, boehmite, akdalaite, bayerite, etc. Our current focuses are on two targeted questions: 1.) the structure of surface complexation: inner-sphere *versus* outer-sphere; [2] 2.) surface charge effects for adsorption at  $\text{pH} > \text{pH}_{\text{ZPC}}$ , where partially deprotonated sites present on surface, illustrated in Fig. 1. Both geometric structures and energy profiling of adsorption of uranyl at will be reported.



In acidic environment, we have found that the average distance of uranium to equatorial oxygen atoms is  $\sim 2.5 \text{ \AA}$ , in good agreement with extended X-ray absorption fine structure (EXAFS) spectroscopy experiment for acidic environment.<sup>[3,4]</sup> The coordination number of uranyl to surface oxygens dynamically changes, indicating multidentate bonding interactions occurring at a finite temperature. The surface charges have profound effects on the surface complexation by forming stronger surface adsorption with a shorter bond distance to the deprotonated site, suggesting a lower mobility of uranyl in a basic environment.<sup>[5]</sup>

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## Response of epikarst hydrochemical changes to soil $\text{CO}_2$ and weather conditions in Chenqi, SW China

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Karst-related carbon cycle, as a result of water-carbonate rock- $\text{CO}_2$  gas-aquatic organism interactions, significantly affects global carbon budget. Soil  $\text{CO}_2$  is a major chemical driving force for karst process and has significant impact on the water-rock-gas-organism system. However, few studies examined the direct correlations between hydrochemical parameters and soil  $\text{CO}_2$  in epikarst systems.

An epikarst spring system in Chenqi, SW China was chosen to monitor soil  $\text{CO}_2$  concentration and hydrochemical parameters with high-resolution (interval of 15 min.) and to investigate the responses of hydrochemical changes to soil  $\text{CO}_2$  and weather conditions. It was found that both soil  $\text{CO}_2$  and rainfall are major driving forces for karst hydrochemical variations. Soil  $\text{CO}_2$  effect on hydrochemical variations was reflected in all seasonal, diurnal and storm-scales. There was an increasing  $\text{CO}_2$  partial pressure ( $\text{pCO}_2$ ) and electrical conductivity (EC) but a decreasing pH in groundwater caused by the increasing  $\text{CO}_2$  in soil during spring-summer growing season, while a decreasing  $\text{pCO}_2$  and EC but an increasing pH caused by the decreasing soil  $\text{CO}_2$  in autumn-winter dormant season. Similar responses were also found on diurnal scales but with a time lag of a few hours during dry season, showing different groundwater recharge mode as well as the complex supply path (quick flow by conduit or slow flow by fracture). During rainy seasons, hydrochemical variations in epikarst spring were regulated by both dilution and soil  $\text{CO}_2$  effects. Under high-intensity rainfall, the dilution effect was dominant, indicated by a quick decrease in EC, pH and calcite saturation ( $\text{SI}_\text{c}$ ) but a quick increase in  $\text{pCO}_2$ . Contrastly, under low-intensity rainfall, soil  $\text{CO}_2$  effect was dominant, indicated by an increase in EC and  $\text{pCO}_2$  but a decrease in pH and  $\text{SI}_\text{c}$ .

To sum up, this study has shown the high sensitivity and variability of karst process to environmental change, implying that the role of karst process in global carbon cycle needs to be reappraised based on high-resolution monitoring strategy.