

The molecular level mechanisms of quartz dissolution at coupled electrolyte-pH conditions

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Both different pH conditions and electrolyte types have profound influence on the dissolution mechanisms of quartz. This study provides molecular level mechanisms related to the quartz dissolution at coupled electrolytes vs. pH conditions. Under acidic, neutral or basic conditions, with either Ca^{2+} , Mg^{2+} or Na^+ cations, the dissolution mechanisms of Q1 (Si) and Q2 (Si) sites at quartz surface, representing the major dissolution story of quartz, have been carefully studied by high-level quantum chemistry calculation. Large cluster models are used to represent the surface structures of quartz. The M05-2X/6-311+G** level and QST3 method are used to estimate the energy barriers of bond breaking occurring at Q1 (Si) and Q2 (Si) sites under those coupled situations.

Many very interesting points have been found in this study. Electrolytes will largely enhance quartz dissolution for the whole pH range. However, whether electrolytes bond to bridging oxygen (BO) or non-bridging oxygen (NBO) of quartz surfaces is the key factor leading to different quartz dissolution mechanisms. At acidic condition, due to the intensive surface protonation, electrolytes are difficult to attack the oxygen atoms of quartz. The dissolution increase is not directly caused by electrolytes but by water which is prone to be electrolyzed at such situations. At neutral conditions, the electrolytes can directly bond to the BO, let a weaken Si-O_{br} bonding and lead to the increase of dissolution. The Ca-O_{br} and Mg-O_{br} bonding are stronger than that of Na-O_{br}, leading to the dissolution rate differences of these electrolytes. At basic conditions, electrolytes cannot link to BO but rather link to NBO, which also cause the dissolution increase. The energy barrier data suggest that the present of electrolytes at neutral or basic conditions will directly and dramatically enhance the quartz dissolution, such as $E_{\text{Ca}}=16$, $E_{\text{Na}}=20$, $E_{\text{Mg}}=48\text{kJ/mol}$ at neutral condition and $E_{\text{Ca}}=11$, $E_{\text{Na}}=8$, $E_{\text{Mg}}=21\text{kJ/mol}$ at basic condition.

Photodegradation of methylmercury is enhanced by complexation with thiol-containing natural organics

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Monomethylmercury (MeHg) is a neurotoxin that poses significant risks to human health due to its persistence in aquatic ecosystems and bioaccumulation in food webs. Sunlight demethylation is an important component of the mercury cycle that maintains MeHg at low concentrations in natural waters. Rates of photodemethylation, however, can vary drastically between different bodies of waters for reasons that are largely unknown. Here, we show that photodegradation of MeHg occurs through sunlight sensitization of dissolved natural organic matter (NOM) and that the rate of degradation depends on water composition and constituents that bind CH_3Hg^+ ions. We demonstrate that singlet state oxygen ($^1\text{O}_2$), which is generated by sunlight sensitization of chromophoric NOM, is capable of demethylating MeHg at rates similar to field observations. However, these rates apply only to MeHg species bound to thiol-containing organic ligands such as glutathione, mercaptoacetate, and humic substances. In contrast, CH_3HgCl complexes are unreactive towards $^1\text{O}_2$. Photochemical experiments indicate that binding of CH_3Hg^+ to electron-dense thiolates lowers the excitation energy of the C-Hg bond, making the bond susceptible to attack by electrophiles such as $^1\text{O}_2$. Our results provide an explanation to why photodemethylation is rapid in NOM-rich freshwater lakes, and relatively slow in coastal marine waters where CH_3HgCl complexes dominate methylmercury speciation.