Effect of CO_2 on MoO_4^{2-} adsorption on ferrihydrite

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Introduction

Molybdate (MoO_4^{2-}) adsorption onto ferrihydrite is an important reaction controlling the geochemical cycle of Mo under an oxygenated atmosphere. Previous researchers have demonstrated that this adsorption decreases with increasing pH, especially at pH > 6. Generally, the adsorption experiments were carried out in (semi) closed systems; reactions involving the dissolved gaseous species were not taken into considertation. Here we investigate the effects of dissolved gaseous species, particularly CO_2 and O_2, on MoO_4^{2-} adsorption on ferrihydrite based on two types of experiments.

Experimental

In the first series of experiments, one-litrer of 10 μM Na2MoO4 solution was prepared under the air; the solution, therefore, contained dissolved CO2, O2, and other gases. The solution was then transferred in a glove box where the atmosphere was regulated at T = 25±2 °C, pN2 = 0.8 atm, pO2 = 0.2 atm, and pCO2 = 0. 10 mg of ferrihydrite were added to the solution to initiate the Mo adsorption. The solution was stirred magnetically, and the pH, pe and DO values were continuously monitored by electrodes. 2 mL aliquots of solution were sampled from periodically for determination of Mo and Fe by ICP-MS.

In the second series of experiments, a Mo- and ferrihydrite-bearing solution was continuously reacted with the normal air (pCO2 = ~400 ppm).

Results and Discussion

The adsorption behavior of MoO_4^{2-} on ferrihydrite showed a clear difference depending on the CO_2 content of the atmosphere. When CO_2 was absent in the atmosphere, CO_2 continuously degassed from the solution, causing the pH to increase from 6.0 (at t = 0) to 8.0 (700 hrs). The pe and Mo adsorption values continuously decreased with increasing pH. These characteristics are similar to those obained by previous investigatoirs for CO_2-poor systems. In contrast, in the experiment performed in the air, the pH remained constant at ~6.0 and the MoO_4^{2-} adsorption reached a steady-sate after ~10 hours at a value that was about one third of the MoO_4^{2-} adsorption in CO_2-poor systems. This suggests the importance of CO_2 in the geochemical cycle of Mo.