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Characterization of mercury sorption on hydroxylapatite: Batch studies and microscopic evidence for adsorption

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ABSTRACT

Although previous studies have investigated Hg sorption on various common minerals, there has been limited study of Hg interaction with apatite. In this study, systematic experiments regarding Hg sorption on HAP were performed over a wide range of physicochemical conditions. In the sorption edge experiments, Hg uptake by HAP exhibits a maximum sorption (~90%) at pH 6.0, which rapidly decreases at pH > 6.0. Sorption isotherms are fitted well by Freundlich equations, and the distribution coefficient (K_D) increases in the order of pH 5 > 7 > 9. In both the sorption edge and isotherm experiments, sorption patterns and quantities are minimally influenced by variations in the ionic strength. The results from the kinetic experiments are in good agreement with the pseudo-second-order rate law. The initial sorption rate at pH 9 is much slower than that at pH 5 and 7. During desorption, ~90% of the sorbed Hg is retained at both pH 6.0 and 9.0, which indicates strong bonding of Hg to the HAP surface. Our results suggest that adsorption plays an important role in controlling the initial stage of interactions between Hg and HAP.

1. Introduction

Mercury (Hg) has been the subject of considerable research due to its drastic increases in manufacturing and emissions from coal-burning power plants over the past few decades, as well as its adverse toxicity to ecosystems and humans. Depending on its forms, mercury can exhibit substantially different toxicities [1]. Organic mercury compounds can cross the blood brain barrier and cause neurological damage. However, the toxicity of inorganic mercury salts varies with their solubility. For example, Hg(I) compounds are less soluble and significantly less toxic than Hg(II) compounds. Most stable oxidation states of Hg are Hg(0) and Hg(II), but Hg(I) is relatively unstable in near-surface environments. Hg(II) tends to be prevalent over Hg(0) in well-oxidizing zones of soils and aqueous environments [2].

Interactions of mercury with minerals, such as clays, metal oxides, and sulfides, have been addressed. Hg sorption on these minerals is distinguished from other types of metal sorption in terms of pH dependence. For example, Hg sorption on goethite exhibits a maximum sorption at pH 4.0 [3]. Guerra et al. [4] reported that the removal of Hg(II) by clays consisting of bentonite and kaolinite moderately declines at pH > 4.0. Similar observations for sorption maximums under acidic conditions have also been reported for Hg interactions with other minerals, such as Mn(IV) oxide and SiO_2 [5,6]. Recently, the study of Hg sorption on Fe or Al-bearing minerals indicates that Hg forms inner-sphere complexes on goethite and bayerite but outer-sphere complexation is a possible mechanism for Hg sorbed on γ-alumina [7]. These studies indicate that the fate and transport of mercury is affected by different mineral phases at the mineral–water interface.

Ligands forming complexes with mercury play an important role in controlling Hg sorption on minerals. Forbes et al. [8] reported that hydrolyzed Hg species are the key factor for understanding Hg uptake by iron hydroxide. With a correlation between the adsorption edge of metals on goethite and the pH of hydrolysis, Collins et al. demonstrated that the adsorption edge for Hg(II) occurs at a lower pH than that of other metals, such as Cd(II) and Zn(II) [9]. However, chloride (Cl) strongly forms complexes with Hg and increases its mobility [2]. Upon interaction of Hg with minerals, chloride tends to inhibit Hg sorption and enhance its desorption. Elliott and Huang [10] found that sorption densities of Hg on silica decrease as the Cl concentration increases. Thanabalasingam and Pickering [6] also reported that Hg sorbed on Mn(IV) oxide decreases in the presence of Cl. These observations suggest that Hg species in solution are one of the crucial factors controlling Hg sorption on minerals in various environments.

Hydroxylapatite (HAP, $[Ca_5(PO_4)_3OH]$) is an essential constituent of bone and teeth for vertebrates. Interactions between various metals and HAP have been extensively studied due to the

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importance of those elements in biological functions. It has been shown that exposure to metals, such as Pb and Hg, can be detrimental to bone health [11,12]. Lead can be toxic because it biologically accumulates in bone tissues. Hg is also known to directly act on bone cell functions, and chronic exposure to Hg causes serious damage to bone. HAP has also been considered an excellent sorbent for toxic metals [13,14]. The removal of metals by apatite derived from animal remains is effective even though the partitioning of metals to HAP is directly affected by physicochemical conditions, such as pH and surface charge [15–18].

Despite the crucial role of hydroxylapatite for the environmental and physiological control of toxic elements, few studies have addressed Hg interactions with HAP. Oliva et al. conducted column experiments with biogenic HAP to evaluate its efficiency for removing Hg in acidic conditions [19]. They found that pH has a strong influence on the removal and that mercury could precipitate as $Hg_3(PO_4)_2$. We are not aware of any other studies that systematically address Hg interaction with HAP.

In this study, we investigated Hg sorption on HAP under different conditions (i.e., pH, ionic strength, initial Hg loading concentration, ligand, and contact time). Our results indicate that an Hg sorption maximum is reached under weakly acidic conditions. In addition, the Hg sorption and desorption on the HAP surface are significantly affected by the presence of Cl.

2. Materials and methods

2.1. Materials and reagents

A Hg stock solution was prepared using $HgCl_2$ and $Hg(NO_3)_2$ (Sigma Aldrich) dissolved in deionized water (>18 mΩ). This stock solution was used for all of the experiments. Hg concentrations of 1, 3, 5, 7, 10, 13, and 20 μM were used in this study. The HAP used for all of the batch experiments was a reagent-grade tribasic calcium phosphate (Mallinckrodt), which was characterized by X-ray diffraction (XRD) and a multipoint BET isotherm using $N_2(g)$. All of the XRD peaks were identified as belonging characteristic of HAP, and the BET surface area of the HAP was 60.4 m^2/g.

2.2. Speciation calculations

For our experimental conditions, the aqueous Hg(II) species and saturation index with respect to various solid phases were calculated by PHREEQC with the minteq.v4 database. The data for the dissolved species and solids of Hg were also supplemented with equations compiled by Clever et al., which are listed in Table 1 [20]. The results from the speciation calculation are shown in Fig. 1. The fractions of individual mercury species and the concentrations of total dissolved Ca and P are sensitive to variations in the pH of the solutions.

Table 1
Stability constants (log *K*) used for aqueous Hg(II) speciation calculations (from Clever et al. [20]).

	Log *K*
$Hg(OH)_2^0 + H^+ + CO_3^{2-} = Hg(OH)CO_3^- + H_2O$	10.59
$Hg(OH)_2^0 + 2H^+ + PO_4^{3-} = HgPO_4^- + 2H_2O$	21.82
$Hg(OH)_2^0 + 3H^+ + PO_4^{3-} = HgHPO_4 + 2H_2O$	27.37
$(HgOH)_3PO_{4(s)} + 4H^+ = 3Hg^{2+} + HPO_4^{2-} + 3H_2O$	−9.4
$Hg_3(PO_4)_{2(s)} + 2H^+ = 3Hg^{2+} + 2HPO_4^{2-}$	−24.6

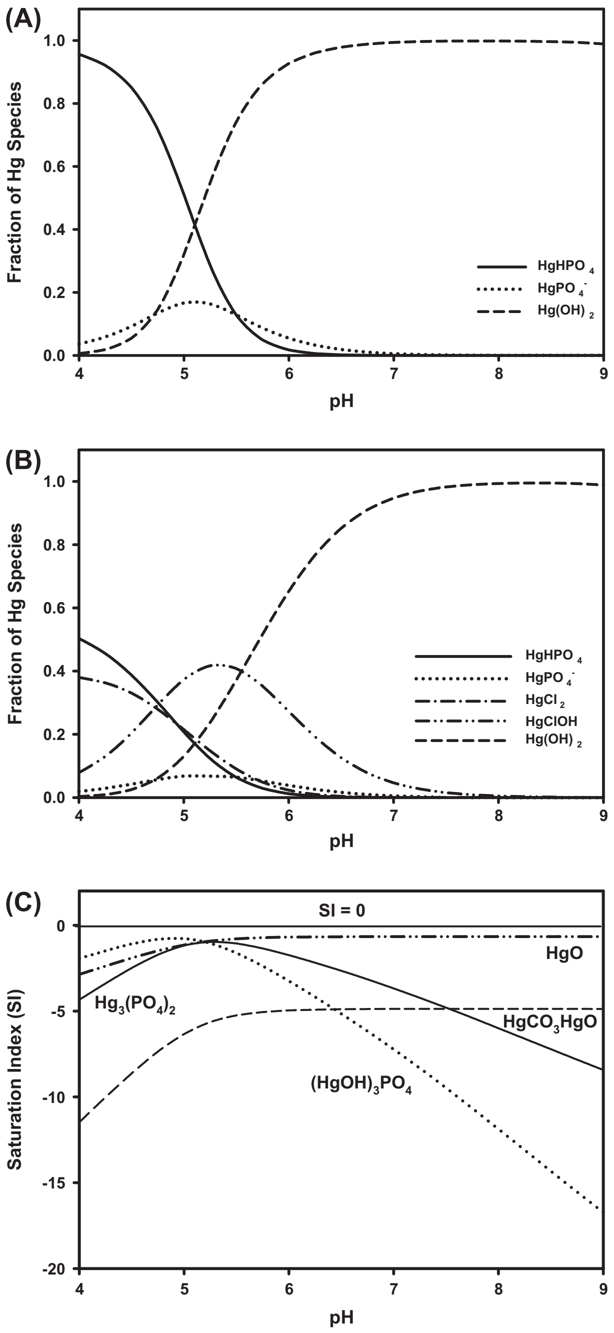

Fig. 1. Hg speciation calculation with 10 μM (A) $Hg(NO_3)_2$ and (B) $HgCl_2$ as a function of pH, and (C) calculated saturation index with respect to various solid phases as a function of pH ($[Hg]_{tot}$ = 50 μM, *I* = 0.01 M $NaNO_3$).

2.3. Batch experiments

Suspensions of 1 g L^{-1} HAP were equilibrated at atmospheric CO_2 pressure ($10^{-3.5}$ bar) for 2 weeks while maintaining pH 4–9 via the addition of HNO_3 or NaOH. The final ionic strengths were adjusted by $NaNO_3$ over the range of 0.01–0.7 M. In all of experiments, Hg was added to the HAP suspensions pre-equilibrated at the desired pH values. Teflon bottles were used to prevent Hg from being sorbed on the wall of the bottle. In addition, Hg was added to a pre-equilibrated solution without HAP for each set of experiments as a control sample. After adding Hg, the suspensions were equilibrated on a reciprocal shaker table for the 24 h sorption experiments at 120 osc/min and ambient temperature. The desorption