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Ion-Exchange Properties of Strontium Hydroxyapatite under Acidic Conditions

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SHIGERU SUGIYAMA,* HITOSHI NISHIOKA,
TOSHIHIRO MORIGA, and HIROMU HAYASHI
DEPARTMENT OF CHEMICAL SCIENCE AND TECHNOLOGY
FACULTY OF ENGINEERING
THE UNIVERSITY OF TOKUSHIMA
MINAMIJOSANJIMA, TOKUSHIMA 770, JAPAN

JOHN B. MOFFAT
DEPARTMENT OF CHEMISTRY AND THE GUELPH-WATERLOO CENTRE
FOR GRADUATE WORK IN CHEMISTRY
UNIVERSITY OF WATERLOO
WATERLOO, ONTARIO N2L 3G1, CANADA

ABSTRACT

The ion exchange of strontium hydroxyapatite (SrHAp) with Pb^{2+} has been investigated under acidic conditions at 293 K. The addition of various acids to the exchanging solution enhanced the exchange capacity in the order HCl > HBr > HF > HNO_3 > no acid, corresponding to the formation of halogen apatites with the former three acids or hydrogen phosphate with HNO_3. Since the ion-exchange capacity of SrHAp under nonacidic conditions is higher than that of chlorapatite, the aforementioned observations can be attributed to the participation of the protons introduced by the acids.

INTRODUCTION

Calcium hydroxyapatite (CaHAp) is an important inorganic solid which is a principal constituent in human calcified hard tissues such as bones and teeth. Since CaHAp can absorb a variety of divalent cations from an aqueous

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* To whom correspondence should be addressed.

acidic solution at temperatures as low as 25°C, the ion-exchange properties of these materials have attracted considerable attention for a number of years (1–14). Suzuki and co-workers suggested that divalent cations with an ionic radii less than that of calcium and an electronegativity greater than that of Ca^{2+} can be ion exchanged into CaHAp (2, 9). More recently the ion-exchange properties of strontium hydroxyapatite [SrHAp; stoichiometric form, $Sr_{10}(PO_4)_6(OH)_2$] were reported (15). Since the radius of Sr^{2+} is larger than that of Ca^{2+} while their electronegativities are similar, SrHAp was expected to display more advantageous ion-exchange properties than CaHAp. As expected, SrHAp with various Sr/P ratios has exchange properties for a number of divalent cations, in particular Pb^{2+}, which are superior to those of CaHAp, the exchange capacity of which is enhanced in the presence of HCl due to the formation of chlorapatite during the exchange process (15). Furthermore, extended x-ray absorption fine structure (EXAFS) analyses revealed that the ion-exchange characteristics were strongly influenced by the nearest-neighbor distances of the Sr—O bond of SrHAp or the Ca—O bond of CaHAp (15).

The present work examines the exchange of Sr^{2+} by Pb^{2+} in SrHAp with an Sr/P of 1.60 in nonacidic and acidic solutions of HCl, HF, HBr, and HNO_3 at 293 K. X-ray absorption near edge structure (XANES) analyses are also employed to provide information on the apatite structure in the Sr^{2+} and Pb^{2+} neighborhoods during ion exchange. In order to examine the contribution of HCl to the ion-exchange properties of SrHAp, SrClAp is also prepared and tested.

EXPERIMENTAL

Materials

All chemicals were of high purity and were used as supplied. SrHAp was prepared from $Sr(NO_3)_2$ (Wako Pure Chemicals, Osaka) and $(NH_4)_2HPO_4$ (Wako) according to a procedure previously described (15–18). The resulting solids were calcined at 773 K after drying in air at 373 K overnight. The Sr/P atomic ratio of SrHAp was 1.60 as determined by ICP. SrClAp was prepared from the pretreatment of SrHAp (3 g) with tetrachloromethane (TCM, 0.51 kPa) diluted with helium for 2 hours at 773 K.

Ion-Exchange Procedure

Each apatite (0.4 g) was stirred at 120 rpm with 100 mL of a 12.5, 25, or 50 mmol/L aqueous solution containing Pb^{2+} in the form of the nitrate at 293 K. In the experiments with added acid, 100 mL of aqueous HCl, HF, HBr, or HNO_3 solution (27 mmol/L) was employed. After a specified period of time, the supernatant solutions and/or the apatite dissolved in HNO_3 solutions were analyzed by ICP (Shimadzu ICPS-5000) or ion chromatography (Shimadzu PIA-1000).

Characterization

The surface areas were measured with a conventional BET nitrogen adsorption apparatus (Shibata P-700). Powder x-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X diffractometer, using monochromatized CuKα radiation. Patterns were recorded over the $2\theta = 5$–$60°$ range. XANES near the Pb L_3 and Sr K edges were measured (2.5 GeV) at the National Laboratory for High-Energy Physics with a storage ring current of ca. 320 mA. The x-rays were monochromatized with channel-cut Si(311) crystals, and the absorption spectra were observed using ionization chambers in a transmission mode. The gas mixture in the ion chamber detector was as follows: $I_0 = 75\%\ N_2 + 25\%\ Ar$, $I = 100\%\ Ar$, and $I_0 = 85\%\ N_2 + 15\%\ Ar$, $I = 50\%\ N_2 + 50\%\ Ar$ for the SrK edge and the Pb L_3 edge, respectively. The sample diluted with BN was compressed into a 13-mm diameter disk. The photon energy was scanned in the range 12.5–14.1 keV for the Pb L_3 edge and 15.8–17.1 keV for the Sr K edge.

RESULTS AND DISCUSSION

Bulk Properties of Prepared Strontium Hydroxyapatite

The surface areas and compositions of the calcined apatites are shown in Table 1. The surface area of SrClAp is smaller than that of SrHAp due to further calcination during the pretreatment with TCM. Although stoichiometric strontium hydroxyapatite (Sr/P = 1.67) should contain 6.77 mmol Sr/g, the measured Sr content of each apatite is somewhat lower. The XRD patterns of SrHap matched that of $Sr_{10}(PO_4)_6(OH)_2$ (JCPDS 33-13248) while that of SrClAp showed that the apatite consisted of $Sr_{10}(PO_4)_6Cl_2$ (JCPDS 16-0666) together with a trace of the hydroxyapatite (see below).

TABLE 1
Bulk Properties of Fresh Apatites

Apatite	Surface area[a]	Sr content[b]	P content[b]	Cl content[b]	Sr/P[c]	Cl/P[c]
SrHAp	67.9	5.49	3.43	—	1.60	—
SrClAp	11.0	5.49	3.43	1.27	1.60	0.37

[a] BET surface area (m^2/g).
[b] By ICP (mmol/g).
[c] Atomic ratio.

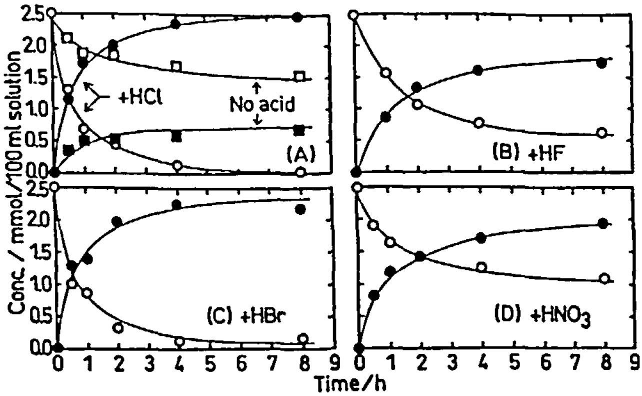

FIG. 1 Effects of the introduction of HCl (A), HF (B), HBr (C), and HNO_3 (D) on the ion-exchange of SrHAp with Pb^{2+} at 293 K. Exchange conditions: 0.4 g SrHAp 100 mL solution containing 27 mmol/L of each acid (when present), and 25 mmol/L Pb $(NO_3)_2$. (●, ■): mmol of Sr^{2+} in 100 mL acidic and nonacidic solutions, respectively. (○, □): mmol of Pb^{2+} in 100 mL acidic and nonacidic solutions, respectively.

Ion Exchange of SrHAp with Pb^{2+} under Acidic Conditions

Ion exchange at 293 K of SrHAp (0.4 g) with 100 mL of nonacidic, HCl, HF, HBr, or HNO_3 (each acid 27 mmol/L) solutions containing 25 mmol/l Pb^{2+} showed that the exchange capacity in the acidic solutions was greater than that in the nonacidic solution (Fig. 1). The exchange capacities with the various solutions followed the order HCl > HBr > HF > HNO_3. The direct ICP analyses of the apatites after the ion-exchange process also support the order of ion exchangeability (Table 2). The detection of a significant quantity

TABLE 2
Atomic Ratio of Pb/Sr after the Ion-Exchange of SrHAp with Pb^{2+}

	Ion-exchange time (h)				
Acid	0.5	1	2	4	8
None	0.159	0.223	0.216	0.232	0.263
HCl	1.31	2.31	2.88	10.8	46.2
HF	0.882	0.688	1.47	1.95	2.60
HBr	0.756	1.02	3.42	7.64	5.99
HNO_3	0.333	0.525	0.924	1.06	1.66

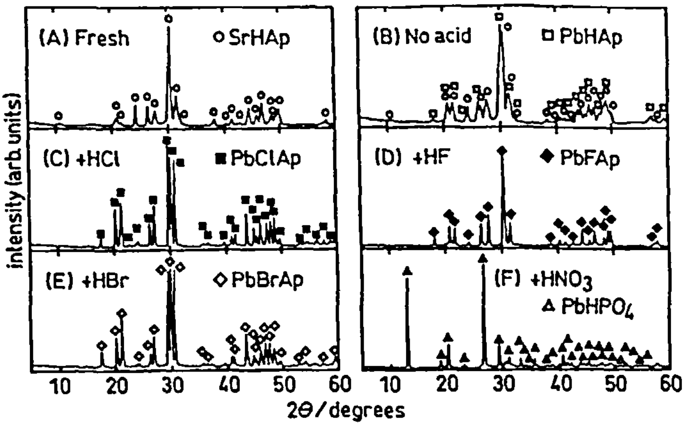

FIG. 2 XRD patterns of fresh SrHAp (A) and those employed in obtaining the results reported in Fig. 1 but in nonacidic (B), HCl (C), HF (D), HBr (E), and HNO_3 (F) solutions after 8 hours, respectively.

of Sr-containing compounds by ICP in contrast to their absence in XRD patterns (particularly Figs. 2C–2E), shows that the Sr species are amorphous. The quantities of Pb^{2+} lost from the solution are approximately equal to those of Sr^{2+} gained in nonacidic, HCl, HF and HBr solutions, as expected for the ion-exchange process, while those of Pb^{2+} are smaller than those of Sr^{2+} due to the dissolution of SrHAp into the HNO_3 solution employed for analytical purposes (17, 18). After evaporation to dryness of the HNO_3 solution of SrHAp, the resulting solid was identified as $SrHPO_4$ by XRD (JCPDS 33-1335, not shown). XRD patterns of fresh SrHAp matched those of JCPDS data (Fig. 2A), while those of SrHAp employed for ion exchange in nonacidic or HCl solution show that the quantity of lead hydroxyapatite or chlorapatite formed during the ion-exchange process increases with the duration of contact time (not shown). After 8 hours the SrHAp ion exchanged in a nonacidic solution became a mixture of SrHAp and $Pb_{10}(PO_4)_6(OH)_2$ (PbHAp, JCPDS 8-0259) while that in HCl solution was completely converted to $Pb_{10}(PO_4)_6Cl_2$ (PbClAp, JCPDS 19-0701) as shown in Figs. 2(B) and 2(C), respectively. However, XRD patterns of SrHAp employed for ion exchange in HF and HBr solutions were not dependent on contact time after 30 minutes and matched those of $Pb_{10}(PO_4)_6F_2$ (PbFAp, JCPDS 23-0348) and $Pb_{10}(PO_4)_6Br_2$ (PbBrAp, JCPDS 32-0553), as shown in Figs. 2(D) and 2(E), respectively. According to the results shown in Fig. 1, in which the supernatant solution was analyzed, compounds including the Sr^{2+} species should be

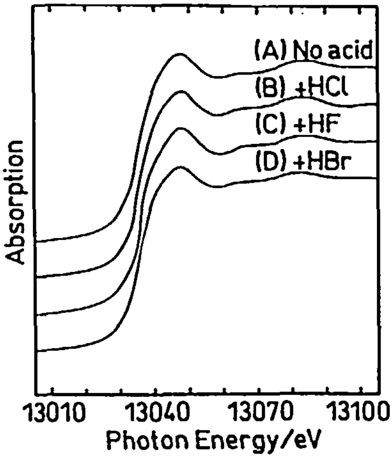

FIG. 3 XANES spectra near PbL_3 edge of SrHAp employed in obtaining the results reported in Fig. 1 but in aqueous (A), HCl (B), HF (C), and HBr (D) solutions after 8 hours, respectively.

detected in each apatite employed in the ion exchange, even in HF and HBr solutions. Indeed, Sr^{2+} species were detected by ICP in each apatite ion-exchanged in these acids (Table 2), indicating that the Sr^{2+} species become amorphous during the ion-exchange process. In contrast to XRD patterns of SrHAp ion-exchanged in HCl, HF, and HBr solutions, that in HNO_3 solution initially showed the formation of $PbHPO_4$ (JCPDS 29-0773) and PbHAp together with unconverted SrHAp (not shown) until finally the apatite was completely converted to $PbHPO_4$ (Fig. 2F). As described above, the OH groups in SrHAp exchanged with halogens concurrently with the cation exchange in HCl, HF, and HBr solutions. However, since the XRD patterns of SrHAp stirred in the acidic solutions for 15 minutes in the absence of Pb^{2+} were similar to those of the original apatite, the anion and cation processes are evidently not additive.

In order to provide information on the changes of the local structure of divalent cations during ion exchange, XANES measurements near the Sr K edge of fresh SrHAp and Pb L_3 edge of SrHAp after ion exchange in non-acidic, HCl, HF, and HBr solutions have been performed. Figure 3 shows XANES spectra near the Pb L_3 edge of SrHAp employed in the ion exchange for 8 hours. The shapes of the XANES spectra and the edge position of Pb^{2+} together with that of Sr^{2+} (not shown) for each apatite are virtually identical, indicating that the electronic configurations and site symmetries of the lead in the four apatites are not significantly different under differing acidic conditions.

Effect of the Initial Concentrations of Pb^{2+} and SrHAp on Ion Exchange in HCl Solution

The effect of changes in the initial concentrations of Pb^{2+} in the exchanging solution has been examined (Figs. 4A and 4B, cf. Fig. 1A). With an HCl solution which is initially equimolar in Pb^{2+} with the Sr^{2+} contained in SrHAp, equimolar quantities of Pb^{2+} and Sr^{2+} are lost and gained, respectively, by the solution (Fig. 1A). A similar result is also observed with a solution containing a 2/1 ratio of Pb^{2+} to the moles of Sr^{2+} contained in SrHAp (Fig. 4B). In contrast, with an HCl solution containing a deficit of Pb^{2+} relative to that of Sr^{2+} in SrHAp, the loss of Pb^{2+} from solution is approximately one-half the increase in Sr^{2+}, indicative of the partial dissolution of SrHAp in the acidic solution. Further experiments showed that hydroxyapatite gradually dissolved in each of the HF, HCl, and HBr solutions where no Pb^{2+} was present. After evaporation to dryness, the solid remaining from the first two of these solutions was identified as $SrHPO_4$ while that from the latter could not be identified. These results suggest that the ion-exchange process occurs sufficiently more rapidly than the dissolution process to either prevent or reduce dissolution in the presence of Pb^{2+} in aqueous solution.

Ion Exchange of SrClAp with Pb^{2+}

As described above, the ion-exchange capacity of SrHAp with Pb^{2+} was enhanced by the addition of HCl, HBr, and HF, resulting in the formation of

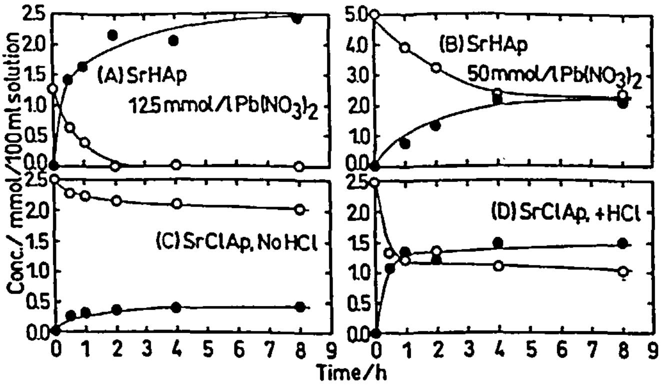

FIG. 4 Effects of the concentration of Pb^{2+} on the ion-exchange of SrHAp and the contribution of SrClAp to the ion-exchange with Pb^{2+} at 293 K. (A) and (B): 0.4 g SrHAp, 100 mL HCl solution (27 mmol/L) containing 12.5 and 50 mmol/L $Pb(NO_3)_2$, respectively. (C) and (D): 0.4 g SrClAp, 100 mL solution in the absence and presence (27 mmol/L) of HCl, respectively, containing 25 mmol/L $Pb(NO_3)_2$.

the corresponding halogen apatites. However, the ion-exchange capacity of SrClAp with Pb^{2+} in the absence of HCl (Fig. 4C) was evidently smaller than that of SrHAp under the corresponding conditions. Therefore halogen apatites formed during ion exchange with Pb^{2+} in the presence of hydrogen halides are apparently not responsible for the observed enhancement of the ion-exchange capacity by the aforementioned halides. When HCl was present during the exchange of SrClAp with Pb^{2+}, the capacity was again enhanced as shown in Fig. 4(D). The enhancement of the ion exchange of SrHAp with Pb^{2+} in the acids is evidently attributable to the protons introduced rather than to the haloanions or the products formed from the latter. It is important to note that the ion-exchange properties are directly influenced by those of the bulk but not those of the surface. Therefore, the observed differences in the surface areas of the apatites have no direct influence on the ion-exchange properties.

CONCLUSION

1. The ion-exchange capacities of strontium hydroxyapatite with Pb^{2+} increase on addition of HCl, HF, HBr, and HNO_3 to the exchange solution with the formation of the corresponding halogen apatites in the former three acids and the loss of the apatite structure in HNO_3.
2. Although SrHAp is soluble in aqueous solutions of particular compositions, in the presence of Pb^{2+} the formation of insoluble lead apatite occurs more rapidly than the dissolution process of the original apatite.
3. The increase in the ion-exchange capacity of SrHAp on addition of HCl can be attributed to the proton and not to the formation of chlorapatite.

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