The adsorption of plutonium IV and V on goethite

ARTHUR L. SANCHEZ[1,3], JAMES W. MURRAY[1] and THOMAS H. SIBLEY[2]

[1] School of Oceanography, University of Washington, Seattle, WA 98195
[2] School of Fisheries, University of Washington, Seattle, WA 98195
[3] Present address: Graduate School of Public Health, University of Pittsburgh, Pittsburgh, PA 15261

Abstract—The adsorption of Pu(IV) and Pu(V) on goethite (αFeOOH) from NaNO₃ solution shows distinct differences related to the different hydrolytic character of these two oxidation states. Under similar solution conditions, the adsorption edge of the more strongly hydrolyzable Pu(IV) occurs in the pH range 3 to 5 while that for Pu(V) is at pH 5 to 7. The adsorption edge for Pu(V) shifts with time to lower pH values and this appears to be due to the reduction of Pu(V) to Pu(IV) in the presence of the goethite surface. These results suggest that redox transformations may be an important aspect of Pu adsorption chemistry and the resulting scavenging of Pu from natural waters.

Increasing ionic strength (from 0.1 M to 3 M NaCl or NaNO₃ and 0.03 M to 0.3 M Na₂SO₄) did not influence Pu(IV) or Pu(V) adsorption. In the presence of dissolved organic carbon (DOC), Pu(V) reduction to Pu(IV) occurred in solution. Pu(IV) adsorption on goethite decreased by 30% in the presence of 240 ppm natural DOC found in Soap Lake, Washington waters. Increasing concentrations of carbonate ligands decreased Pu(IV) and Pu(V) adsorption on goethite, with an alkalinity of 1000 meq/l totally inhibiting adsorption.

The Pu-goethite adsorption system provides the data base for developing a thermodynamic model of Pu interaction with an oxide surface and with dissolved ligands, using the MINEQL computer program. From the model calculations we determined equilibrium constants for the adsorption of Pu(IV) hydrolysis species. The model was then applied to Pu adsorption in carbonate media to see how the presence of CO_3^{2-} could influence the mobility of Pu. The decrease in adsorption appears to be due to formation of a Pu-CO₃ complex. Model calculations were used to predict what the adsorption curves would look like if Pu-CO₃ complexes formed.

INTRODUCTION

ADSORPTION ONTO suspended particulate matter has been suggested as the major removal mechanism for plutonium from natural waters. This removal process is thought to affect Pu in freshwater, estuarine, and marine environments, regardless of whether its source is bomb fallout Pu, accidentally released Pu, or Pu introduced with low-level radioactive wastes (see *e.g.* BOWEN *et al.*, 1980). Many workers have argued that this observation is due to the interaction of the strongly hydrolyzable Pu(IV) oxidation state with the surfaces of natural particulate matter. Thermodynamic calculations, however, show that Pu(V) is the stable oxidation state in the pH range of 5 to 7 at a pE of 12 and that Pu(VI) should be the most stable oxidation state at higher pH values. Pu(IV) is predicted to be stable only below pH 5 (SANCHEZ, 1983). Recent analyses support these calculations and suggest that the dominant oxidation state of Pu in oxygenated surface waters is the oxidized Pu(V) or Pu(VI) state (*e.g.*, NELSON and LOVETT, 1978, 1981; NELSON and ORLANDINI, 1979; BONDIETTI and TRABALKA, 1980). In such environments, Pu removal to the sediments must be explained by more than simple adsorption of the IV oxidation state.

There are few rigorous laboratory studies of the adsorption of actinides or of strongly hydrolyzable cations in general. Some of the early work on Pu focused on its interactions with soils (*e.g.*, PROUT, 1957; RHODES, 1957). Distribution coefficient studies (*e.g.*, DUURSMA and PARSI, 1974; GROMOV and SPITSYN, 1974; BONDIETTI *et al.*, 1976; SANCHEZ *et al.*, 1982) used water and sediments from various locations to determine the partitioning of Pu between sediment particles and water. While such studies are useful in developing predictive models for Pu distribution in a particular environment, the adsorbent and the solution phases are much too complex to provide a straightforward interpretation of the adsorption data. We choose to use simpler, better-defined experimental systems to obtain data that could be readily interpreted using adsorption equilibrium models. There have been few equivalent studies. ROZZELL and ANDELMAN (1971) characterized the sorption behavior of Pu(IV) on various silica surfaces. Clay minerals have also been used in some experiments (*e.g.*, BONDIETTI *et al.*, 1976; DE REGGE *et al.*, 1980; BILLON, 1982).

In this paper, the results of experiments to determine the effects of pH, ionic strength, alkalinity, and dissolved organic carbon on the adsorption of Pu on goethite are presented. Two oxidation states of plutonium, Pu(IV) and Pu(V), were used in these experiments. The results of environmental studies in Saanich Inlet and Soap Lake (SANCHEZ *et al.*, in press) were used as important criteria for determining the range of the variables used in the laboratory experiments.

METHODS

All experiments were carried out at room temperature (20 ± 2°C) in borosilicate glass vessels. Chemicals used were ACS analytical reagent grade. Water was distilled, demineralized and passed through 0.22 μm Nuclepore filters prior to use in the experiments.

A. Plutonium tracer

Two oxidation states of the isotope Pu-238 ($t_{1/2}$ = 88 yr), obtained from the Oak Ridge National Laboratory, were prepared for the experiments. The method recommended by FOTI and FREILING (1964) for the preparation of Pu(IV) and Pu(VI) was used. Briefly, Pu(IV) was prepared by first evaporating the tracer solution to dryness with hydroxylamine-HCl to reduce all Pu to the III state. The residue was then dissolved in 1 M HNO_3 with a few crystals of $NaNO_2$ added to oxidize Pu(III) to the IV state. Pu(VI) was prepared by evaporating the tracer solution to dryness with concentrated HNO_3, and dissolving the residue with 0.05 M $HClO_4$ containing 0.005 N $K_2Cr_2O_7$. After adding Pu(VI) to our adsorption media, it was readily reduced to Pu(V).

The techniques of solvent extraction in TTA-xylene, lanthanum fluoride coprecipitation, adsorption on silica gel, and $CaCO_3$ coprecipitation were used to characterize the Pu oxidation states in our tracer spike solutions and in our adsorption experiments (SANCHEZ, 1983). An organic phase containing 0.5 M 2-thenoyltrifluoroacetone (TTA) in xylene is selective for ionic Pu(IV) at pH 0.3 or lower, while the Pu(III), (V) or (VI) states are not extracted at this low pH. Lanthanum fluoride coprecipitates Pu(III), (IV) and possibly (V) but not Pu(VI). Pu(VI) adsorbs more strongly than Pu(V) on silica gel while freshly precipitated $CaCO_3$ adsorbs Pu(V) more strongly than Pu(VI). Details of these various techniques for characterizing the oxidation states are described in FOTI and FREILING, 1964; BONDIETTI and REYNOLDS, 1976; MAGNUSSON and LACHAPELLE, 1948; NELSON and LOVETT, 1978, and NELSON and ORLANDINI, 1979. Under the solution conditions of the adsorption experiments the oxidation states Pu(IV) and Pu(V) were confirmed to be present by a combination of these tests (SANCHEZ, 1983). Similar characteristics of these oxidation states were obtained by CHOPPIN and MORSE (in press).

B. Adsorption

The synthetic goethite (αFeOOH) used in these experiments was prepared using the method of ATKINSON et al. (1967). The surface characteristics of αFeOOH prepared with this procedure have been studied extensively (ATKINSON et al., 1967; BALISTRIERI, 1977; BALISTRIERI and MURRAY, 1981, 1982).

The adsorption experiments included the following steps: (1) preparation of the solid suspension in a borosilicate glass vessel; (2) addition of the Pu tracer; (3) immediate adjustment of pH with either 0.1 N HCl or 0.1 N NaOH; (4) equilibration of the spiked suspensions after adjusting the total volume to 20.0 ml; (5) measurement of pH prior to sampling; (6) determination of Pu partitioning between dissolved (<0.45 μm) and adsorbed phases by filtering a subsample from each vessel and counting both dissolved and particulate fractions for Pu activity; and (7) oxidation state measurements for selected samples. Variations of this general procedure were used to test the effects of pH, ionic strength, carbonate alkalinity, and dissolved organic carbon on the adsorption behavior of both Pu oxidation states on αFeOOH. A time series of subsamples were collected from each experimental vessel until equilibrium distribution of Pu between the soluble phase and the solid phase was attained. The goethite concentration was 28.5 m^2l^{-1}. A blank electrolyte solution identical to the experimental medium but containing no αFeOOH was run in parallel with the adsorption solutions to correct for adsorption on the vessels. No attempts were made to shield these experiments from light. It appears that the rates of adsorption may be different under light and dark conditions (KEENEY-KENNICUTT and MORSE, in press).

1. Effect of pH on Pu adsorption. Each point on the adsorption *versus* pH plots represents one experimental vessel. The background electrolyte was 0.1 M $NaNO_3$. Adsorption experiments were run using both Pu(IV) and Pu(V) initial spike solutions.

In a separate set of experiments with Pu(V), samples were collected for solvent extraction into TTA-xylene to determine if Pu(V) had been reduced to the TTA-extractable Pu(IV) state (SANCHEZ, 1983). Two series of experiments for each oxidation state (IV and V) were performed using 1×10^{-11} M and 1×10^{-10} M ^{238}Pu.

2. Effect of ionic strength on Pu adsorption. Three different electrolytes at the following concentrations were used in these experiments: 0.1 M, 0.5 M, 1.0 M and 3.0 M $NaNO_3$; 0.5 M and 3.0 M NaCl; and 0.03 M, 0.15 M and 0.30 M Na_2SO_4. The range in ionic strengths for NaCl and $NaNO_3$ and the sulfate concentrations were chosen to approximate values observed for Soap Lake surface and monimolimnion waters. Soap Lake is an alkaline, meromictic lake in Eastern Washington state, where we have measured relatively high concentrations of Pu compared to other natural waters (SANCHEZ, 1983). All experiments were at pH 7.0 ± 0.2, 28.5 m^2 αFeOOH l^{-1}, and Pu(IV) and (V) concentrations of 1×10^{-11} M.

3. Effect of carbonate alkalinity on Pu adsorption. Appropriate volumes from a 1.0 M $NaHCO_3$ stock solution were added to distilled, deionized water to prepare adsorption media with the following total alkalinities: 10, 30, 100, 200, 400, 500, 700, and 1000 meq/L. No attempt was made to maintain a constant ionic strength for these adsorption media and the solutions were open to the atmosphere. The pH 8.6 ± 0.1 and total Pu concentration was 10^{-11} M ^{238}Pu(IV or V). Blanks were run along with the experiments to determine if Pu(V) was reduced to Pu(IV) in carbonate media and to correct for adsorption on the vessels. Filtered (0.22 μm) water from 12 m and 24 m in Soap Lake were also used to determine Pu adsorption under natural Soap Lake conditions. The anoxic sample from 24 m was left to equilibrate with air until all H_2S was oxidized prior to use in the experiments. It must be pointed out that these samples from Soap Lake may also contain potential Pu ligands, such as dissolved organic carbon, in addition to the carbonate species.

4. Effect of dissolved organic carbon (DOC). Two sets of experiments were performed using the naturally-occurring DOC concentrations in Soap Lake surface and monimolimnion waters. Water from 12 m and 24 m were acidified by dropwise addition of concentrated HCl until all the CO_2 was removed (pH < 4). DOC measurements for these acidified samples were done on a Dohrman DC-80 Total Organic Carbon Analyzer system.

In the first experiment, ^{238}Pu(V) tracer was added to a set of samples from 12 m at a concentration of 1×10^{-11} M, and the pH readjusted to pH 4 and 6 using 0.1 N NaOH solution. Filtered Soap Lake water (not degassed) from 12 m was also used as an experimental medium, with its pH constant at 9.8. An additional experimental vessel containing humic acid extract from Washington continental shelf sediments (DOC = 100 ppm, pH 9.6) was also included in this series. One ml subsamples were analysed to determine if Pu(V) was reduced to Pu(IV) in these media using solvent extraction in TTA/xylene (SANCHEZ, 1983).

A second set of experiments was conducted to determine the adsorption of ^{238}Pu(IV) (1×10^{-11} M) at various concentrations of DOC. Varying proportions of the acidified (pH 3.8) surface and bottom samples from Soap Lake were combined to obtain a range of DOC values. The pH was then adjusted to pH 7.1 ± 0.1. The pH was left at 7 because buffers for other pH values could complex Pu and confuse our results.

C. Radioactivity measurements

Liquid scintillation counting was used to measure the [238]Pu activity in all samples. Ten ml of a commercially prepared counting cocktail, 3a70B, (Research Products International Corp., Elk Grove Village, Illinois) were added to 4 ml of aqueous sample adjusted to an acidity of 0.5 N HCl. For organic samples from TTA-xylene extraction, 10 ml scintillation mixture were added directly without acidification. No quenching was observed in the acid phase or the TTA-xylene organic phase, as checked with internal [238]Pu standards prepared in either 0.5 N HCl or TTA-xylene extractant. An internal [238]Pu standard prepared in acid solution containing goethite had showed similar counts as a standard in acid solution alone. A Packard TriCarb Model 3375 Liquid Scintillation Spectrometer was used for counting samples.

RESULTS AND DISCUSSION

1. Kinetics of Pu(IV) and Pu(V) adsorption

Two observations distinguish Pu(IV) from Pu(V) adsorption on αFeOOH: (1) rapid kinetics for Pu(IV) adsorption compared to Pu(V), and (2) a significant difference in their initial adsorption edges under similar solution conditions. Equilibrium adsorption for Pu(IV) on αFeOOH is attained within one hour (Fig. 1a) and the adsorption edge occurs from pH 3 to 5. Under similar experimental conditions, Pu(V) does not attain equilibrium distribution even after 20 days, and the adsorption edge gradually shifts from pH 7 to lower pH values (Figs. 1b and 1c).

The observed shift in the adsorption edge for Pu(V) and its slow adsorption kinetics appear to be inconsistent with thermodynamic calculations which predict that Pu(V) is stable under the conditions of these experiments (SANCHEZ, 1983). The gradual increase in Pu(V) adsorption with time, caused its adsorption edge to approach that for Pu(IV), suggesting that Pu(V) may be reduced to the lower oxidation state. This was tested experimentally by investigating the solvent extraction behavior into TTA/xylene of the adsorbed and soluble Pu fractions. Any significant removal of Pu into the organic phase under the low pH extraction conditions indicates the presence of the Pu(IV) oxidation state.

The amount of TTA-extractable Pu as a function of time in the adsorbed and the soluble fractions of goethite experiments spiked initially with Pu(V) is shown in Fig 2. The initial time points are for 1 hour after adsorption. The data show that soluble Pu remained unextracted (<5%) into TTA-xylene with time, indicating that no significant reduction of Pu(V) to Pu(IV) occurred in solution. This observation is further supported by TTA analyses of corresponding blank solutions (no αFeOOH added), where no extraction into TTA-xylene was found. Thus, Pu(V) remained as this oxidation state in solution. In contrast, the goethite-absorbed Pu showed increasing extraction into TTA-xylene with time. However, at the low pH (<3.8) where Pu(V) did not adsorb, no extraction into the TTA phase was observed. These observations suggest two possibilities: (1) Pu(V) is reduced to Pu(IV) following its adsorption on goethite, or (2) Pu(V) close to the goethite surface is reduced to Pu(IV), with the Pu(IV) sub-
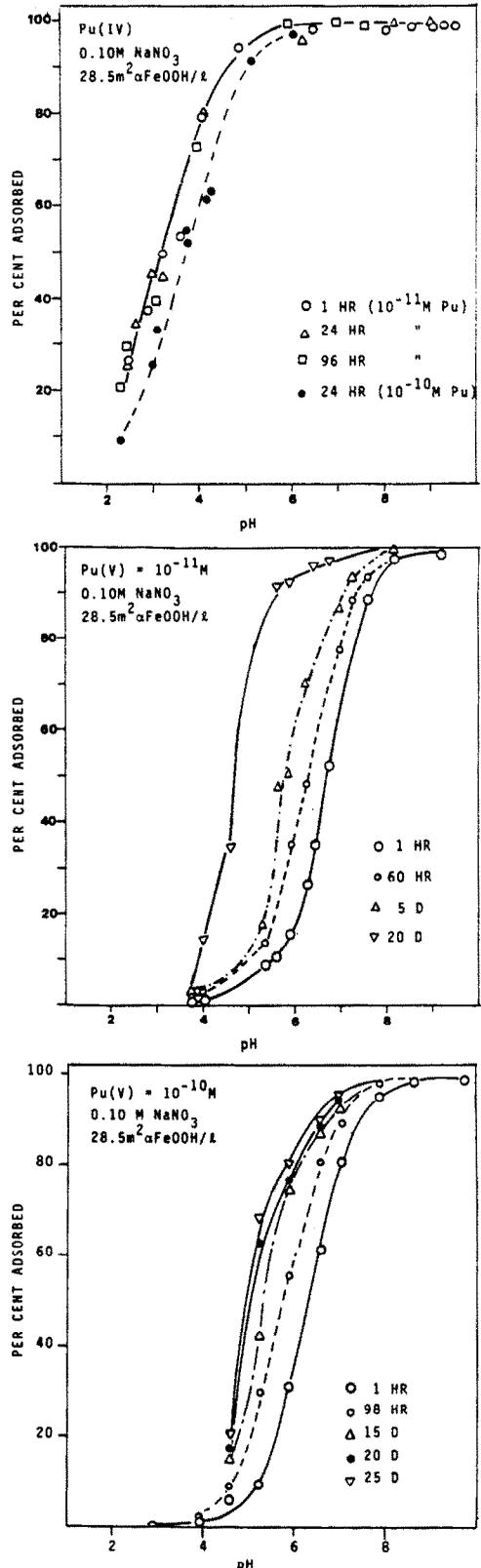
FIG. 1. a) Adsorption of Pu(IV) on goethite as a function of pH from 0.1 M $NaNO_3$ solution at two plutonium concentrations (10^{-11} and 10^{-10} M). b) The adsorption of Pu(V) on goethite as a function of pH from 0.10 M $NaNO_3$ solution at 10^{-11} M. c) Adsorption of Pu(V) on goethite as a function of pH from 0.10 M $NaNO_3$ solution at 10^{-10} M.
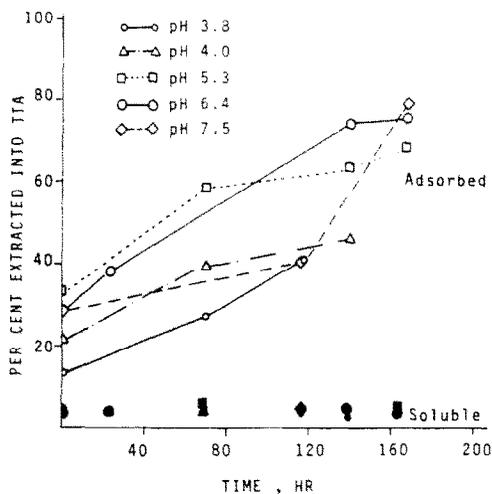
FIG. 2. The percent of total Pu(V) added that became TTA-extractable Pu(IV) as a function of time in the adsorbed and the dissolved fractions. Results from goethite experiments initially spiked with Pu(V). Initial data points are for 1 hour after adsorption started. Error for TTA extraction is ±5%.

sequently rapidly adsorbed. The data are not sufficient to distinguish which of these two mechanisms is occurring. However, recent observations of KEENEY-KENNICUTT and MORSE (1985) indicate that Pu(V) adsorbs as this oxidation state on a variety of mineral surfaces. Their results would support the first mechanism to account for our observations, particularly since we found that no reduction occurs when Pu(V) is not adsorbed.

Three possibilities may be suggested to account for the observed reduction of Pu(V) after adsorption: (1) thermodynamic data are wrong and Pu(IV) is the stable form under the pH conditions of our experiments (pH 5 to 7). (2) trace amounts of reducing agents are present on the goethite surface; or (3) the reduction of Pu(V) occurs via a radiolysis or disproportionation reaction. If Pu(IV) is really the stable oxidation state the implication is that Pu(V) is reduced slowly by water when it is immobilized by adsorption. Pu(V) in homogeneous solutions is kinetically stable and is not reduced for indefinite time periods. It was not possible to determine the presence of trace amounts of reducing agents in the experiments. Given the small concentrations of Pu used, however, it is conceivable that any trace constituent occurring as an impurity in the media may potentially act as a reducing agent. There is the more unlikely possibility that as soon as the radioactivity becomes concentrated on the solid surface, the production of reducing agents such as H_2O_2, OH radicals and nitrite (MINER and SEED, 1967) via the radiolysis mechanism becomes important. The concentrations of these species would probably be too small to be detected because of the minimal radioactivity in the experiments. The final possibility is the reduction of Pu(V) via the disproportionation reaction, whereby

Pu(IV) and Pu(VI) species are produced (CONNICK, 1949; RABIDEAU, 1957). KEENEY-KENNICUTT and MORSE (in press) invoked this mechanism to account for the reduction of Pu(V) to Pu(IV) in their goethite adsorption experiments.

2. Effect of pH on Pu(IV) and Pu(V) adsorption

The major difference between the adsorption of Pu(IV) and Pu(V) is in the position of their initial pH adsorption edges under similar solution conditions (I = 0.1 M $NaNO_3$). In Fig. 1a, the adsorption edge for Pu(IV) occurs at the pH range 3 to 4, in contrast to that for Pu(V) (Figs. 1b and 1c), which has an initial adsorption edge between pH 6 to 7. The pH of the adsorption edge for Pu(V) is a lower limit because of the uncertain role of Pu(V) reduction to Pu(IV). The one hour data are probably a close approximation.

The difference in the adsorption edge is possibly linked to the tendency of these ions to hydrolyze in solution. BALISTRIERI et al. (1981) found a linear correlation between the apparent adsorption equilibrium constant for metal adsorption on goethite and the hydrolysis constants of that specific metal ion. The larger the hydrolysis constant, the stronger the adsorption and the lower the pH of the adsorption edge. Pu(IV) (in the ionic form Pu^{4+}) is the most strongly hydrolyzed and Pu(V) (as PuO_2^+ ion) the least hydrolyzed among the common oxidation states of Pu in aqueous solutions. The observed difference in their initial adsorption edges is therefore consistent with their different hydrolytic character.

Another observation is the shift in the adsorption edges to slightly higher pH range with increased Pu concentration for each oxidation state (Figs. 1a, b, and c). This is similar to the results of BALISTRIERI and MURRAY (1982) for Cu, Pb, Zn, and Cd adsorption on goethite as a function of the metal concentration and may be due to strong binding site limitation. This suggests that adsorption of Pu rather than its precipitation on the goethite surface is the controlling mechanism.

We proceeded to model the adsorption versus pH data. We first determined adsorption equilibrium constants to enable us to predict Pu adsorption in different environments. The same constants are used later to estimate the values of dissolved Pu-carbonate complexes.

In recent years, several electrostatic models have been developed for describing ion adsorption at the oxide/water interface (see WESTALL and HOHL, 1980, for a review of these various models). Our adsorption experiments on goethite were designed so that the results could be interpreted using the site-binding or triple layer model. This model has already been successfully applied by BALISTRIERI and MURRAY (1981, 1982) for the adsorption of major ions and trace metals on goethite and this was the main reason it was used in this study. Other models exist that would also fit the data

equally well. This model was applied to our Pu adsorption data using the MINEQL computer program (WESTALL et al., 1976).

The details of the site-binding model, and the theoretical and experimental work that went into deriving the various parameters used to describe the goethite surface, will not be discussed here. The reader is referred to YATES et al. (1974), DAVIS et al. (1978), WESTALL and HOHL (1980), and BALISTRIERI and MURRAY (1981) for details. Briefly, the site-binding model assumes a structure of the electrical double layer which can be described mathematically by a set of adjustable physical parameters. BALISTRIERI and MURRAY (1981) have presented the experimental data used for defining goethite interactions in simple electrolyte systems. Their model parameters for the surface area, the total number of surface sites, the inner and outer layer capacitances, the surface hydrolysis constants of goethite and the surface complexation constants for Na^+ and NO_3^- are used here.

Modelling the Pu adsorption data as a function of pH involves defining the intrinsic surface complexation constants for Pu interaction with the goethite surface. Four reactions involving the adsorption of Pu(IV) hydrolysis species were required to describe the adsorption of Pu(IV).

$$SOH + Pu^{4+} + 2H_2O \overset{*K^{INT}_{Pu(OH)_2^{2+}}}{\rightleftharpoons} SO^-Pu(OH)_2^{2+} + 3H^+$$

$$SOH + Pu^{4+} + 3H_2O \overset{*K^{INT}_{Pu(OH)_3^+}}{\rightleftharpoons} SO^-Pu(OH)_3^+ + 4H^+$$

$$SOH + Pu^{4+} + 4H_2O \overset{*K^{INT}_{Pu(OH)_4^0}}{\rightleftharpoons} SO^-Pu(OH)_4^0 + 5H^+$$
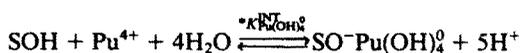
In these equations, SOH represents a surface site, and the $*K^{INT}$ is the intrinsic constant describing Pu association with goethite. The values of the log $*K^{INT}$ that were required to fit the adsorption data were 2.50, −2.00 −5.90 and −12.0 for $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(OH)_3^+$ and $Pu(OH)_4^0$ respectively. The incremental addition of these constants to produce a model best fit is shown in Fig. 3. In this way the effect of the addition of each reaction on the final model curve can be seen. The values are a unique set and are accurate to at least 0.5 log units. The hydrolysis constants for Pu(IV) reported by METIVIER and GUILLAUMONT (1976) were used in these calculations. (BAES and MESMER, 1976; CHOPPIN, 1983). Although these constants were obtained at slightly higher ionic strengths (I = 1.0 M), no corrections were made for ionic strength in our model calculations. It should be clearly stated that there are still some uncertainties in the hydrolysis constants for Pu(IV) and the values for $*K^{INT}$ depend on the hydrolysis constants used in the calculations. These uncertainties are not large enough to invalidate our general conclusions.

The data for Pu(V) were not interpreted using MINEQL modelling because an equilibrium distribution was not attained. It was uncertain whether Pu(V) remained stable in the experiments. In addition, the hy-
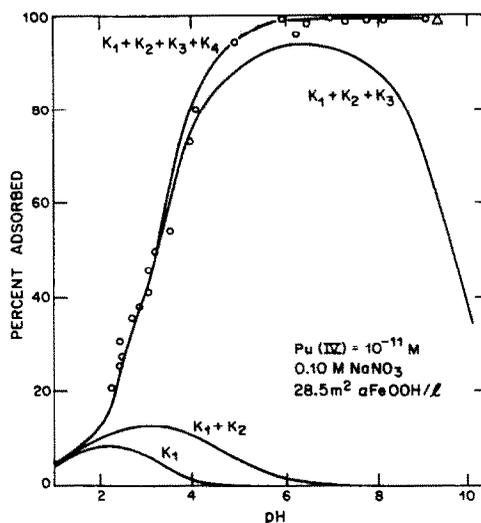
FIG. 3. Adsorption of Pu as a function of pH on goethite. Four reactions for the adsorption of Pu(IV) hydrolysis species are required to model the data (circles). The incremental addition of these reactions to the equilibrium program MINEQL to produce a model best fit is shown.

drolysis constants for Pu(V) are even less well known than those for Pu(IV).

3. Effect of ionic strength on Pu adsorption

Changes in ionic strength do not appear to exert a major control on the adsorption of either Pu(IV) or Pu(V). The adsorption of $^{238}Pu(IV)$ and $^{238}Pu(V)$ on $\alpha FeOOH$ did not vary with increasing ionic strength (up to I = 3) at pH 7.0 ± 0.2, regardless of the background electrolyte. As summarized in Table 1, greater than 90% of the total activity for both oxidation states is found on the goethite phase after equilibrium distribution is attained. Sulfate ion did not influence adsorption of either Pu(IV) or Pu(V) up to 0.3 M SO_4^{2-} although it is one of the known complexing agents for Pu (CLEVELAND, 1979). Enhancement of Pu adsorption due to SO_4^{2-} as seen for Cu and Zn adsorption on goethite (BALISTRIERI and MURRAY, 1982) could not be identified in these experiments because we were in the greater than 90% adsorption range.

4. Effect of carbonate alkalinity

The adsorption of $^{238}Pu(IV)$ and $^{238}Pu(V)$ on $\alpha FeOOH$ as a function of increasing alkalinity is plotted in Figs. 4a and 4b. The experiments were open to the atmosphere. The pH values for the individual vessels were constant at about pH 8.60 ± 0.10 during the course of the experiments. The lower curve in each plot represents adsorption data after 1 hour of equilibration; the upper curve is for the "true" equilibrium adsorption points (96 hours for Pu(IV) and ~300 hours for Pu(V)). Adsorption of both oxidation states is unaffected by alkalinity values less than about 100 meq/

Table 1. Adsorption of $^{238}Pu(IV)$ and V on $\alpha FeOOH$ as a function of ionic strength, pH 7.0 ± 0.2, Pu_{total} = 1×10^{-11} M.

Electrolyte Solution	Oxidation States	% Adsorbed at Equilibrium
0.1 M NaNO$_3$	IV	97±3
	V	93±3
0.5 M NaNO$_3$	IV	97±3
	V	94±3
1.0 M NaNO$_3$	IV	98±3
	V	97±3
3.0 M NaNO$_3$	IV	98±3
	V	93±3
0.5 M NaCl	IV	98±3
	V	96±3
3.0 M NaCl	IV	97±3
	V	97±3
0.03 M Na$_2$SO$_4$	IV	97±3
	V	93±3
0.15 M Na$_2$SO$_4$	IV	97±3
	V	95±3
0.30 M Na$_2$SO$_4$	IV	95±3
	V	93±3

L, where the amount adsorbed on $\alpha FeOOH$ is similar to that obtained at the same pH in 0.1 M NaNO$_3$ solution. The effect of alkalinity, however, becomes progressively more important for alkalinity values greater than 100 meq/L, and adsorption is totally inhibited at a concentration of 1000 meq/L. The adsorption from natural filtered Soap Lake water at alkalinities of 144 meq/L (pH = 9.8) and ~1200 meq/L (pH = 9.5) are shown in the same plots. At equilibrium, the amounts of Pu IV and V adsorbed onto goethite in these Soap Lake media agree with the expected removal based on alkalinity alone. However, it must be pointed out that the filtered Soap Lake water contains potential Pu ligands other than the carbonate species, such as dissolved organic carbon, that may also influence Pu adsorption behavior. The effects of organic carbon will be discussed later.

At equilibrium, the adsorption versus alkalinity plots for both Pu(IV) and Pu(V) overlap (Figs. 4a and 4b). This suggests that either the adsorption behavior of Pu(IV) and Pu(V) under high carbonate concentrations are similar or that there is a redox transformation of one oxidation state to another. To test this hypothesis, solutions of both Pu(IV) and (V) in high carbonate media in the absence of solid were taken for solvent extraction with TTA-xylene.

The Pu(IV) tracer in 1.0 M NaHCO$_3$, at pH 8.6 in the absence of $\alpha FeOOH$, remained in the soluble (<0.45 μm) fraction but only 50% of the total activity in solution could be extracted into TTA after 300 hours (Table 2). This observation suggests that although Pu(IV) remained filterable, only 50% was in the ionic form which can be extracted into TTA. In a less concentrated carbonate medium (0.03 M NaHCO$_3$, pH 8.6), increasing amounts of non-extractable Pu (<0.45 μm), presumably polymeric species of Pu(IV), were

found with time. This suggests that hydrolysis is important in this medium and that carbonate complexing can not compete effectively with the formation of hydrolytic Pu(IV) species. BONDIETTI et al. (1976) observed that polymeric Pu was formed and absorbed to the walls of the reaction vessel in 0.1 M NaHCO$_3$ solution at pH 8.0. At the Pu concentration (~10^{-8} M) which they used in their experiments, they concluded that carbonate ions are unable to stabilize a Pu(IV) monomeric complex.

Similar tests with the Pu(V) oxidation state showed that it remained soluble and did not extract significantly into TTA in either the 1.0 M NaHCO$_3$ or the 0.03 M NaHCO$_3$ blank solutions (no goethite present) (Table 2). Pu(V) appeared to be stable in this oxidation state at these solution conditions. In the presence of $\alpha FeOOH$, the amount of TTA-extractable Pu in the soluble fraction increased with time. In one experiment (1.0 M NaHCO$_3$, pH 8.6), to which Pu(V) was initially added, only 2 to 4% of the total Pu adsorbed and 93% of the soluble fraction was extracted into TTA after 300 hours (Table 2). These observations indicate that in the presence of the adsorptive surface, Pu(V) is reduced to Pu(IV). This reduction was also observed in the pH experiments but in that case, Pu(IV) remained on the solid. Here, it appears that the complexation of Pu(IV) by carbonate ligands removes the adsorbed Pu. This provides further evidence that Pu(V) reduction occurs in the presence of goethite. Thus, the similarity in the sorption plots for Pu(IV) and Pu(V) versus increasing alkalinity is due to the reduction of Pu(V) to Pu(IV) in the presence of the oxide surface followed by complexation with carbonate ions.

In the carbonate experiments, three possible factors are likely to be influencing the Pu distribution: (1) adsorption onto the goethite surface, (2) hydrolysis of Pu, and (3) carbonate complexing. We have attempted a preliminary interpretation of our data using the site-binding model including all three interactions. In the preceding section, an adsorption model that sufficiently described the adsorption behavior of Pu(IV) as a function of pH was developed. An extension of this model to include carbonate complexing was then carried out. We will show here how the formation of such complexes could possibly influence the adsorption of Pu(IV). This model can be refined as the thermodynamic data is improved.

The formation of dissolved Pu(IV)-CO$_3$ complexes is poorly understood (CLEVELAND, 1979; KIM et al., 1983). MOSKVIN and GEL'MAN (1958) attempted to determine the formation constants for Pu(IV)-CO$_3$ complexes by measuring the solubility of Pu(OH)$_4$ (am) at pH 11.5 in concentrated K$_2$CO$_3$ solutions. They assumed that the complex PuCO$_3^{2+}$ was formed by the reaction:

$$Pu^{4+} + CO_3^{2-} = PuCO_3^{2+}$$
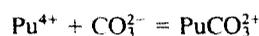
and estimated the formation constant to vary from 10^{34} to 10^{42}. SCHWAB and FELMY (1983) reviewed this
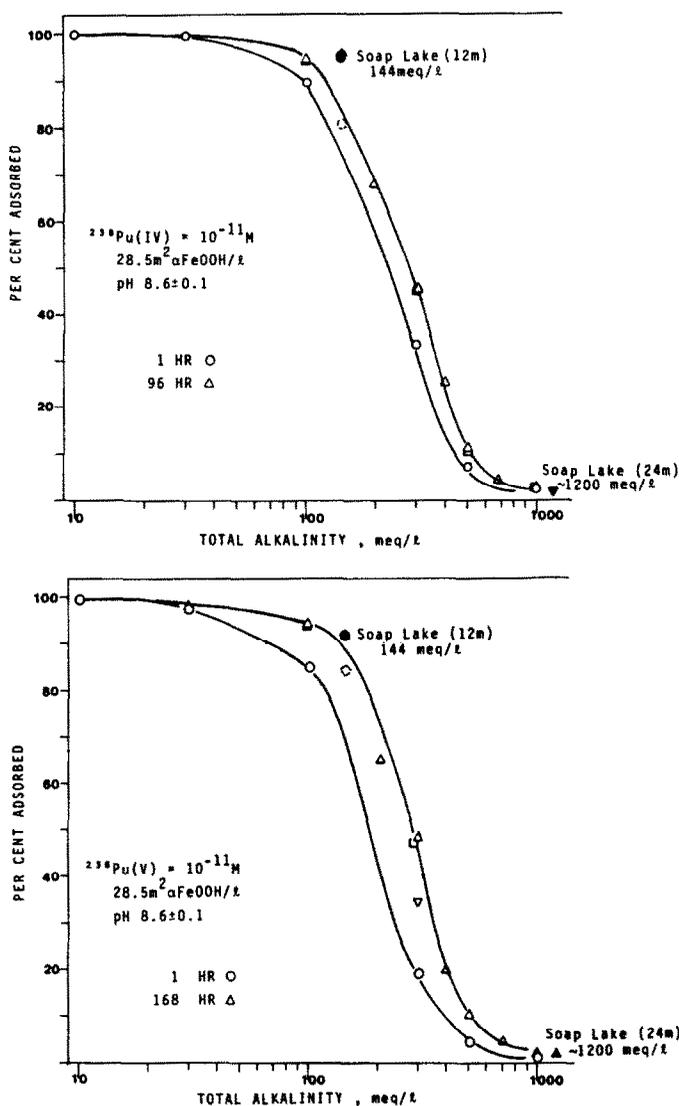
FIG. 4. a) The effect of carbonate alkalinity on the adsorption of Pu(IV) on goethite. b) The effect of carbonate alkalinity on the adsorption of Pu(V) on goethite. Adsorption from natural Soap Lake water is also shown. (Solid symbols).

data set and proposed that the main species is probably a mixed hydroxy-carbonate complex formed by the reaction:

$$Pu^{4+} + 4H_2O + CO_3^{2-} = Pu(OH)_4CO_3^{2-} + 4H^+$$
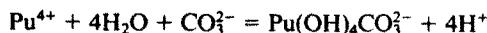
with $\log K = -4.1 \pm 1.0$. From a coordination chemistry point of view the species $Pu(OH)_4CO_3^{2-}$ seems unlikely. A third possibility that has not been explored is that a CO_3^{2-} ligand could replace one OH^- to form $Pu(OH)_3CO_3^-$. The formation of the species $PuCO_3^{2+}$, $Pu(OH)_4CO_3^{2-}$ and $Pu(OH)_3CO_3^-$ were added to the model and tested using MINEQL. In addition we assumed that the carbonate ions interact with the surface of goethite as described by BALISTRIERI and MURRAY (1982):

$$SOH + CO_3^{2-} + H^+$$

$$= SOH_2^+CO_3^{2-} + H_2O \quad \log K_{CO_3}^{INT} = 15.90$$

$$SOH + CO_3^{2-} + 2H^+$$

$$= SOH_2^+HCO_3^- + H_2O \quad \log K_{HCO_3}^{INT} = 22.30.$$
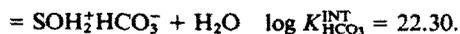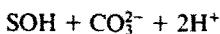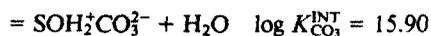
We also assumed that the intrinsic adsorption constants derived previously for Pu(IV)-goethite interaction are still valid.

In our first calculations we assumed that a Pu(IV)-CO$_3$ complex forms and that these species do not adsorb. The formation of either $PuCO_3^{2+}$ or $Pu(OH)_4CO_3^{2-}$ with the formation constants cited above would result in no adsorption under the conditions of our experiments (curve A). This model is clearly inconsistent with our experimental data (curve

Table 2. Characteristics of Pu(IV) and (V) tracers in NaHCO₃ solution. $Pu_{total} = 10^{-11}$ M.

Oxidation state	NaHCO₃, M	Method	Results
Pu(IV)	1.0 M, pH 8.6	TTA extraction	filterable through 0.45 μm filter 50% in TTA
Pu(IV)	0.03 M, pH 8.6		15% retained on 0.45 μm filter after 24 hr.
Pu(V)	1.0 M, pH 8.6	TTA extraction	filterable through 0.45 μm filter 2% in TTA
Pu(V)	0.03 M, pH 8.6	TTA extraction	filterable through 0.45 μm filter 3% in TTA
Pu(V)	0.03 M, pH 8.6 with αFeOOH	TTA extraction of soluble fraction	87% in TTA after 100 hr.
Pu(V)	1.0 M, pH 8.6, with αFeOOH	TTA extraction of soluble fraction	93% in TTA after 300 hr.

FIG. 5. Adsorption equilibrium model fits to adsorption *versus* alkalinity data (curve D) of Pu(IV) on goethite. The curves represent the following conditions. a) Formation constant for $Pu(OH)_4CO_3^{2-}$ is log $K = -4.1$ or for $PuCO_3^{2+}$ is log $K = 34$. b) Formation constant for $Pu(OH)_4CO_3^{2-}$ is log $K = -7.2$ or for $Pu(OH)_3CO_3^-$ is log $K = +1.40$ or for $PuCO_3^{2+}$ is log $K = +27.2$. c) Formation constant for $Pu(OH)_4CO_3^{2-}$ is log $K = -4.1$ and the adsorption equilibrium constant for $Pu(OH)_4CO_3^{2-}$ is log $K = 15.6$.

D). We then tested the possibility that the formation constants are too large. We varied the formation constants until the % adsorbed was about 50% at an alkalinity of 300 meq l⁻¹. Then we varied the alkalinity to generate the curve. Because the formation of each of the three species considered involves only one CO_3^{2-}, the effect of all three species is the same (curve B). The log formation constants for $PuCO_3^{2+}$, $Pu(OH)_4CO_3^{2-}$ and $Pu(OH)_3CO_3^-$ would have to be $+27.2$, -7.1, and $+1.40$ respectively. The formation constants for $PuCO_3^{2+}$ and $Pu(OH)_4CO_3^{2-}$ would be weaker than those previously estimated. Regardless of whether these are reasonable constants the formation of these species would not result in a steep enough dependency of % adsorbed on alkalinity. Adding complexes with two or more carbonate ligands (e.g., $Pu(CO_3)_2^0$) would make the curve steeper.

We also tested what the distribution would look like if the dissolved $Pu(OH)_4CO_3^{2-}$ species could adsorb. SCHINDLER (1981) reviewed some of the experimental evidence for the formation of "ternary surface complexes" (i.e., complexes that participate in a surface reaction) and suggested that these complexes should not be ignored in model calculations which consider the effects of dissolved ligands. We assumed that the formation constant for $Pu(OH)_4CO_3^{2-}$ is accurate and that this species adsorbs on the surface of goethite according to:

$$Pu^{4+} + SOH + CO_3^{2-} + 4H_2O$$

$$= SOH_2^+ Pu(OH)_4CO_3^{2-} + 3H^+.$$

The curve C in Fig. 5 corresponds to this example with an intrinsic adsorption constant of log $K_{Pu(OH)_4CO_3^-}^{INT}$ = 15.6. The alkalinity dependency of this curve is a much closer representation of the experimental data.

Though there are some uncertainties in the adsorption models one point is clear and that is that increasing

alkalinity above 100 meq l⁻¹ can decrease the adsorption of Pu(IV) and Pu(V). This appears to be due to the formation of Pu-CO₃ complexes. Model profiles suggest that the best fit to the data will be when Pu-CO₃ complexes form and then form a ternary complex with the goethite surface.

5. Effect of dissolved organic carbon (DOC) on Pu adsorption

The naturally-occurring DOC in Soap Lake water reduced Pu(V) to the IV oxidation state, as indicated
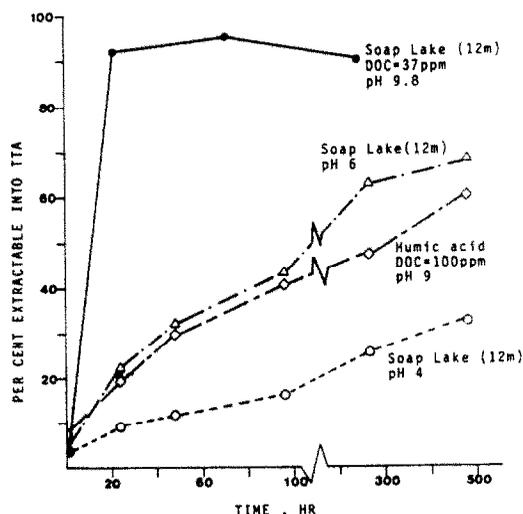
FIG. 6. The kinetics of Pu(V) reduction to TTA extractable Pu(IV) in Soap Lake water samples containing the naturally-occurring dissolved organic carbon fraction in the lake water. Humic acid extract is used as a reference organic material.

by its increased extraction into TTA/xylene with time (Fig. 6). The rate of reduction increased with increasing pH, and was fastest in the non-degassed Soap Lake sample at pH 9.8. A humic acid extract from Washington continental shelf sediments was also found to reduce Pu(V) (Fig. 6). These results are similar to those obtained by NASH et al. (1981) for Pu(VI) reduction by humic acids in NaHCO₃ solution. These laboratory observations agree with the suggestion of BONDIETTI et al. (1976) that Pu(V) should be unstable to reduction to Pu(IV) in the presence of organic substances. Furthermore, the results suggest that Pu in Soap Lake surface waters should be in the IV oxidation state, in agreement with the observation of WAHLGREN et al. (1978) that Pu(IV) is the dominant oxidation state in eutrophic waters.

Since DOC was found to reduce Pu(V), the effect of DOC on Pu adsorption was studied using only the IV oxidation state. Two observations were noted in these experiments: (1) a much slower approach to equilibrium adsorption compared to the pH experiments, and (2) a slight decrease in adsorption with increasing DOC concentration (Fig. 7). These are similar to results of NELSON et al. (1980, 1981), who found that the distribution coefficient for ²³⁷Pu between sediments and water decreased as the DOC concentration increased.

A simple mathematical model similar to the one we developed for the Pu-goethite-carbonate system was also applied to the adsorption data. The results of our calculations are published elsewhere (SIBLEY et al., 1984). Essentially, we found that a model assuming two different binding sites on DOC as suggested by ALBERTS et al. (1980) and neglecting DOC-goethite interactions reasonably fit the adsorption data.

One major difference between these adsorption data and those obtained at increasing carbonate ion concentrations is that even at the high DOC concentrations
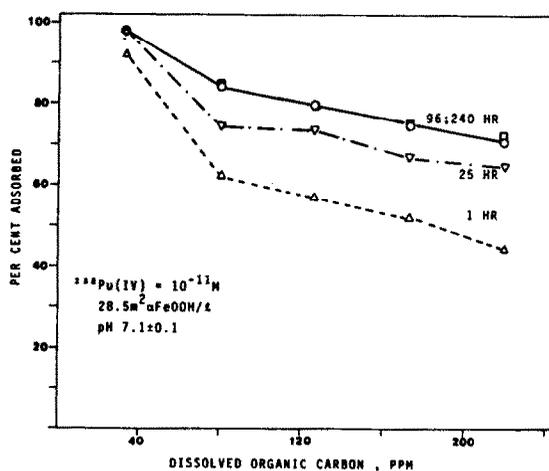
for Soap Lake monimolimnion waters (DOC = 220 ppm), a substantial fraction (70%) of Pu(IV) still adsorbs on goethite. In this same water with greater than 1 M total carbonate concentration, no adsorption on goethite was obtained. These results suggest that carbonate anions inhibit Pu(IV) adsorption on goethite more strongly than DOC at the concentration ranges tested for these ligands. SIMPSON et al. (1980) reached a similar conclusion for Mono Lake.

CONCLUSIONS

1. Under similar solution conditions, the adsorption edge for Pu(IV) occurs at a significantly lower pH range (pH 3 to 5) than for Pu(V) (initially at pH 5 to 7). This result is consistent with the different hydrolytic character of these two oxidation states in aqueous solutions.

2. For Pu(V), a gradual shift in the adsorption edge to lower pH ranges occurs with increasing time of adsorption. Solvent extraction tests with TTA/xylene indicate that the adsorbed Pu(V) has been reduced to the IV oxidation state. Although thermodynamic calculations predict that Pu(V) is stable under the solution conditions of the experiments, it appears that it is unstable to reduction to Pu(IV) in the presence of an adsorptive surface.

3. The triple layer model for the adsorption of Pu(IV) on goethite in NaNO₃ predicts that four hydrolytic species of Pu(IV), $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(OH)_3^+$ and $Pu(OH)_4^0$ adsorb on the goethite surface. The log intrinsic constants for the interaction of these species with the oxide surface that reasonably fit the adsorption data are 2.50, −2.0, −5.9 and −12.0, respectively. Since Pu(V) was unstable in the presence of goethite, the data were not used in the triple layer model calculations.

4. An increase in ionic strength from 0.1 M to 3.0 M NaNO₃ or NaCl did not affect the adsorption of Pu on goethite. Sulfate (0.03 M to 0.3 M) also did not decrease Pu removal on goethite although it is one of the known inorganic complexers for Pu.

5. Pu(V) was reduced to Pu(IV) in solution in the presence of natural dissolved organic carbon (DOC) from Soap Lake. At 240 ppm DOC concentration, Pu(IV) adsorption on goethite was reduced by 30%.

6. Increasing concentrations of carbonate ions decreased Pu(IV) and Pu(V) adsorption on goethite. At a concentration of 1 M NaHCO₃ (pH 8.6) Pu adsorption was inhibited completely. The decrease in adsorption appears due to formation of a Pu-CO₃ complex, however, the value of the formation constant is poorly known and it is also uncertain whether or not the complex adsorbs.

FIG. 7. The effect of dissolved organic carbon from Soap Lake waters on the adsorption of Pu(IV) on goethite. The alkalinity was zero in these experiments.

Soap Lake samples. T. Rasp typed the manuscript. This research was funded by NSF OCE 82-14072.

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