spheric ClO abundance is smaller by at least a factor of 7 than currently accepted values suggests that the role of ClO and chlorofluorocarbons in the destruction of the earth's O_3 layer may need to be reevaluated.

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Neptunium and Americium Speciation in Selected Basalt, Granite, Shale, and Tuff Ground Waters

Abstract. *Neptunium and americium are relatively insoluble in ground waters containing high sulfate concentrations, particularly at 90°C. The insoluble neptunium species is Np(IV); hence reducing waters should enhance its formation. Americium can exist only in the trivalent state under these conditions, and its solubility also should be representative of that of curium.*

Neptunium has been called "the neglected actinide" (*1*), and this characterization could apply to americium as well. Both are present in significant quantities in spent reactor fuel, and both pose potential threats to the environment. The "hazard index" for ^{237}Np, based on half-life, environmental mobility, biological activity, and other factors, has been estimated to equal that of ^{239}Pu (*2*). Nevertheless, in contrast to the case for plutonium, there is a paucity of information on the ground-water chemistry of these two elements. As far as we know, only a few papers on the environmental chemistry of these elements exist (*1*, *3*), even though Foti and Freiling (*4*) did pioneering work in 1959.

Moreover, much of the research on plutonium reactions in ground water has suffered from a failure to determine its oxidation-state distribution and presence in complexes. Without such information for neptunium, the much-needed studies of its ground-water chemistry also are likely to yield meaningless data.

In an effort to correct these deficiencies, we have studied the chemical speciation of neptunium and americium in ground waters associated with rock types proposed as possible hosts for nuclear waste repositories. The four waters were from the Grande Ronde basalt from the Hanford reservation in Washington, Climax stock granite and tuff from the Nevada Test Site, and Cretaceous shale from a rural well near Rapid City, South Dakota. References to the hydrogeology of the sites have been cited (*5*). Their ground-water compositions are shown in Table 1. For comparison, the study also included deionized water. We made no attempt to control the atmosphere above the ground waters during the experiments, because similar studies with plutonium (*5*) had shown that within the time scale of this study the oxidation-reduction behavior of the waters was determined by ionic species rather than by dissolved oxygen.

The general procedure for the addition of neptunium or americium to the waters, equilibrations, and analysis was the same as that for plutonium (*5*). Sufficient ^{237}Np or ^{241}Am in $0.5M$ to $1.0M$ $HClO_4$ solution was added to achieve a concentration of approximately $10^{-8}M$ ($10^{-11}M$ for americium) in the waters; as in the plutonium study, the amount of this solution added was so small that *p*H adjustment after addition was required only in the case of the deionized water. After the specified equilibration periods, the solutions were mixed and sampled, both before and after filtration through 0.05-μm Nuclepore (*6*) filters. The filtrates were subjected to radiometric analysis for total neptunium or americium concentration as well as to praseodymium fluoride (PrF_3) carrier precipitation [for Np(III) and Np(IV) or Am(III)] in the presence of $K_2Cr_2O_7$ holding oxidant added just before HF addition, and thenoyltrifluoroacetone (TTA) extraction [also for Np(IV)], as described (*5*). (Because the tetravalent state was absent, TTA extraction was omitted in the americium study.) Whereas plutonium was extracted with TTA from $1M$ acid, neptunium extraction was found to be most efficient from $0.5M$ acid; otherwise, the procedures used were the same. Neptunium and americium were determined on all samples by radiometric alpha counting.

To assess the effect of initial oxidation state, we conducted separate experiments using reduced [primarily Np(IV)] and oxidized [primarily Np(V)] neptuni-

Table 1. Ground-water compositions (in milligrams per liter).

Solute	Basalt	Granite	Shale	Tuff
Alkalinity (as $CaCO_3$)	146	140	530	98
Calcium	< 0.1	300	100	10
Magnesium	< 1	3	50	3
Sodium	300	300	700	50
Silica	100	10	10	70
Chloride	140	73	61	7
Fluoride	52	0.8	0.1	2.3
Sulfate	75	980	2000	19

um. Also, we carried out all experiments at 25° and 90°C to determine the effect of temperature. In all cases duplicate experiments were conducted; the values shown are the averages of the two replicates. We estimate the accuracy of the data to be within 15 percent, on the basis of the precision of duplicates and the internal consistency of the various fractions.

The neptunium speciation results are shown in Tables 2 and 3. For the ground waters containing added Np(V) (Table 2), essentially all neptunium remained in solution in this oxidation state at both temperatures. The one exception was the shale ground water at 90°C, in which neptunium was slowly, but almost completely, converted to an insoluble form. Neptunium insolubility in this water was surprising in view of the known solubility of Np(V) in near-neutral waters and suggested that perhaps the neptunium in shale ground water was reduced to relatively insoluble Np(IV). To test this possibility, the filters used in two experiments (one for each of the two possible oxidation states) containing a high percentage of insoluble neptunium were washed with 0.5*M* $HClO_4$, and the resulting solutions were passed through the filters and immediately subjected to PrF_3 carrier precipitation and TTA extraction procedures. Essentially all insoluble neptunium on the filters was in the Np(IV) state. Thus, the behavior of Np(V) in shale ground water is similar to that of oxidized plutonium, the principal difference being the rates of reduction. The slower reduction of Np(V) has been observed in other systems (*7*). The identity of the reductant could not be established.

When neptunium was added in the Np(IV) state (Table 3), there was generally lower solubility in several of the ground waters. At 25°C, solubility in shale ground water decreased over 30 days to about half the original value, whereas, in all the other waters tested, 75 percent or more of the neptunium was still in solution over this time period. However, at 90°C, only basalt ground water and deionized water were able to maintain most of the neptunium in solution for 30 days. Solubility was lower in shale ground water, but it was also at a minimum in tuff ground water. In the tuff ground water, formation of the insoluble species began only after 17 days or longer.

Table 4. Percentages of americium in solution at various times [Am(III) was the only oxidation state detected in solution] after addition as Am(III); 100 percent of the americium was present initially as Am(III). Estimated uncertainty, ±15 percent.

Ground water	7 days		27 days	
	25°C	90°C	25°C	90°C
Basalt	67	54	52	50
Granite	98	100	100	100
Shale	59	11	24	20
Tuff	44	56	74	58
Deionized	47	59	48	56

Table 5. Percentage of element (initial concentration, $10^{-8}M$) remaining in solution after 17 days at 90°C.

Element	Basalt ground water	Shale ground water
Np(IV)	94	12
Np(V)	87	16
Pu(III) and Pu(IV)	95	20
Pu(V) and Pu(VI)	94	6
Am(III)	43	8

In our paper on plutonium speciation (*5*), we demonstrated that the plutonium insolubility in shale ground water was the result of the high sulfate concentration in this water, but we were unable to advance a satisfactory explanation for its effect. The same behavior was observed with neptunium in shale ground water; but we would caution as before that sulfate may not have this effect in all ground waters. By contrast, the high solubility of plutonium in basalt ground water was ascribed to complexing by the high concentration of free fluoride ions in this water. Neptunium was also consistently soluble in basalt ground water; however, because it was present as Np(V), which forms only weak fluoro complexes and which is relatively soluble even as an uncomplexed ion, the solubilizing effect of fluoride was minimal. This conclusion is further supported by the observation that Np(V) was equally soluble in deionized water, which contains no fluoride ion.

Speciation data for Am(III), the only oxidation state for americium to be expected in natural waters, are given in Table 4. With the exception of the shale ground-water data at 7 days, the values appear to be substantially independent of temperature. Americium was completely soluble only in granite ground water; approximately half of it was soluble in basalt, tuff, and deionized waters. This order of solubility contrasts with that observed for neptunium and plutonium. The lower relative solubility of americium in basalt ground water reflects the lack of stabilization by fluoride complexing, as does the comparable solubility of americium in deionized water. The solubility of americium in shale ground water paralleled that of neptunium and plu-

Table 2. Percentages of neptunium in solution at various times [Np(V) was the only oxidation state detected in solution] after addition as Np(V); 100 percent of the neptunium was present initially as Np(V). Estimated uncertainty, ±15 percent.

Ground water	1 day		3 days		7 days		17 days		30 days	
	25°C	90°C	25°C	90°C	25°C	90°C	25°C	90°C	25°C	90°C
Basalt	74	81	83	83	79	90	86	87	89	81
Granite	90	90	90	83	92	77	95	88	95	83
Shale	82	59	90	72	90	67	91	16	78	10
Tuff	91	88	93	93	95	77	85	77	95	79
Deionized	88	88	80	89	88	89	94	92	88	91

Table 3. Percentages of neptunium in solution at various times [Np(V) was the only oxidation state detected, except for the two parenthetical values, which are percentages of Np(IV)] after addition as Np(IV); > 99 percent of the neptunium was present initially as Np(IV). Estimated uncertainty, ±15 percent.

Ground water	1 day		3 days		7 days		17 days		30 days	
	25°C	90°C	25°C	90°C	25°C	90°C	25°C	90°C	25°C	90°C
Basalt	80 (23)	95 (10)	96	72	87	94	90	94	79	88
Granite	84	80	85	100	90	75	91	69	89	46
Shale	69	34	73	25	70	16	49	12	50	16
Tuff	80	87	91	95	88	91	85	100	87	12
Deionized	93	98	85	86	87	95	85	100	76	96

tonium; all three of these actinides were least soluble in this water.

Because all actinides in the same oxidation state display similar chemical behavior, the americium results may be assumed to be generally applicable to curium. Application to Pu(III), however, is less certain because of the ease with which this element can be converted to higher oxidation states with different chemical properties.

Because the primary purpose of this study was to compare the abilities of various ground waters to maintain neptunium and americium in solution, we made no attempt to use equal concentrations of the two elements. However, we also compared the behavior of each element in the ground waters, using americium and plutonium concentrations comparable to that of neptunium ($10^{-8}M$). We used only basalt and shale ground waters and sampled the solutions after 17 days at 90°C. The results (Table 5) are very similar to those obtained at lower concentrations and suggest that the reported solubilities are not saturation-limited but are valid over a range of concentrations. All species except Am(III) exhibited similar—and almost complete—solubility in basalt ground water, whereas all were essentially insoluble in shale ground water. The behavior of neptunium was somewhat different at 25°C.

We conclude that mobilization of all four actinides in these ground waters was minimized by reducing conditions and by high concentrations of sulfate ion, but it is uncertain whether the effect of sulfate could prevail in all ground waters. In contrast to the behavior observed for plutonium, the presence of high concentrations of free fluoride had no discernible effect on neptunium and americium solubilities. These characteristics vary with location within any given host rock type, and hence they are site-specific. Because of this, we propose that the chemical composition of the associated ground water and actual speciation experiments be included along with other relevant parameters as criteria in the selection of geologic sites as possible repositories for nuclear waste.

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Inhibitory Role of the Endothelium in the Response of Isolated Coronary Arteries to Platelets

Abstract. *Aggregating autologous platelets caused contraction of isolated rings of canine left circumflex arteries. The contractions were augmented after removal of the endothelium and were attenuated by serotonergic antagonists. During contraction caused by prostaglandin* $F_{2\alpha}$*, aggregating platelets caused a transient increase in tension followed by a profound relaxation of arteries with endothelium, but caused only further contraction of arteries without endothelium. These observations demonstrate the importance of the vascular endothelium in opposing the constriction of coronary vessels caused by 5-hydroxytryptamine and other substances released from aggregating platelets.*

When platelets aggregate, they release a number of substances including 5-hydroxytryptamine (5HT) and thromboxane A_2, both of which can cause contraction of vascular smooth muscle cells (*1*). The endothelial cells play a major protective role by producing prostacyclin which inhibits platelet aggregation (*2*). The permeation of 5HT released from platelets to the smooth muscle cells may be limited by its enzymatic destruction by the monoamine oxidase in the endothelial cells (*3*). In addition, arterial endothelial cells can respond to a variety of agents by causing inhibition of the contractile process of the vascular smooth muscle (*4, 5*). The present study was designed to determine the role of the endothelium in the response of coronary vascular smooth muscle to aggregating platelets and to determine to what extent 5HT released by the platelets can be held responsible for the observed responses.

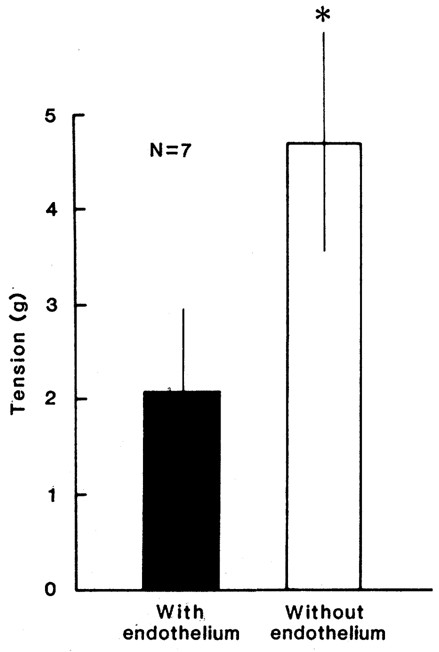

Fig. 1. Influence of endothelium on maximum contractile response of left circumflex artery rings to aggregating platelets. Addition of platelet suspensions resulted in contractions that reached a maximum within 10 minutes. The asterisk indicates a significant difference ($P < .05$) by Student's *t*-test for paired comparisons between arterial rings from the same vessel with and without endothelium. There was no significant difference in the contractions of rings with or without endothelium to $4 \times 10^{-2}M$ potassium chloride (11 ± 0.9 and 11 ± 1.0 g, respectively). To exclude α- or β-adrenergic and cholinergic actions all experiments were performed in the presence of phentolamine, propranolol, and atropine ($10^{-6}M$).

The left circumflex artery was dissected from the heart of mongrel dogs. Paired segments of vessel, 4 mm in length, were cut; in one the endothelium was removed by gentle rubbing of the intimal surface (*4, 5*). Rings were suspended in organ chambers filled with physiological salt solution (4 ml), and isometric tension was measured after equilibration of the rings at the optimal resting tension for contraction (*6*). In each study the integrity of the endothelium was demonstrated by the concentration-dependent relaxations induced by acetylcholine during contraction with prostaglandin $F_{2\alpha}$; no significant relaxation occurred in vessels denuded of endothelium (*7*). Autologous blood was collected in an anticoagulant consisting of acid, citrate, and dextrose. Platelet rich plasma was obtained by centrifugation (180*g* for 10 minutes). A pellet of platelets was obtained (1600*g* for 10 minutes) and resuspended in calcium-free saline containing 0.4 percent citrate at