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**An Autoradiographic Study
of Actinide Sorption on
Climax Stock Granite**

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AN AUTORADIOGRAPHIC STUDY OF ACTINIDE SORPTION ON CLIMAX STOCK GRANITE

G. W. Beall,^{*} G. D. O'Kelley, and B. Allard[†]

ABSTRACT

An autoradiographic technique that employed an arrangement for placing in firm contact Polaroid sheet film, a scintillator screen, and the radioactive face of a specimen was applied to a study of the sorption of americium, neptunium, plutonium, and uranium on Climax Stock granite under varying conditions of pH and Eh. Qualitative agreement was found between the sorption of americium on crushed, pure minerals and on the minerals comprising the specimen of Climax Stock granite. The observations also supported a mechanism for reduction of Np(V) to Np(IV) and Pu(VI) to Pu(IV) by Fe(II)-containing minerals. There was no evidence for reduction of U(VI) by the Fe(II)-containing minerals, although the uranium, assumed to be present as UO_2^{2+} , appeared to be the only actinide species to exhibit sorption by a simple, cation-exchange mechanism at particular mineral sites. Some implications of these results for nuclear waste isolation are discussed briefly.

KEYWORDS: Actinide sorption, Autoradiography, Nuclear waste.

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INTRODUCTION

The sorption of actinides on pure minerals or crushed rocks has been studied by many investigators in connection with various concepts of nuclear waste isolation. Such measurements have usually employed either batch equilibration or column techniques. Two major objections have been raised to the conclusions regarding sorption on whole rocks derived from such experiments. Some investigators have suggested that studies conducted on pure minerals can not be employed to predict the sorption on whole rocks, since factors such as grain boundary and surface area effects are ignored. A second related objection is that, in the past, many studies on crushed rocks which have attempted to correlate certain sorption mechanisms with the individual minerals contained in them have required rather indirect reasoning, with inconclusive results. An example of this latter sort of study is the work of Francis and Bondietti¹ on the reduction of Np and Tc by minerals containing ferrous iron. These questions have prompted this investigation, in which an autoradiographic technique was employed to study the sorption of actinide ions on Climax Stock granite in several groundwater systems, from which qualitative comparisons could be made between literature data on pure minerals and the sorption patterns observed.

EXPERIMENTAL

The Climax Stock granite used in these studies was obtained from R. J. Serne of Battelle Northwest Laboratories in connection with the Waste Isolation Safety Assessment Program. The granite was sawed into slabs approximately 3 cm on an edge and 3 mm thick. The slabs

were polished on a lapidary wheel with corundum polishing compound. Based on sorption measurements on corundum,² the small contamination of the granite by the abrasive would have a negligible effect on sorption of the actinides. Optical photographs were then taken to be used in identification of the mineral components.

All sorption experiments were carried out on the same slab of Climax Stock granite, with final dimensions of 2.7 x 3.1 x 0.3 cm. Before each experiment, the polished face was cleaned with 6 M HCl, followed by washing with distilled water. Occasionally, an additional step of decontamination was included, using a solution of detergent and EDTA. Final repolishing began with grade 180 or 320 emery paper, followed by finer grades of abrasive, and was completed with grade 600 emery paper. The fresh surface was washed with distilled water, dried with tissue, and quickly mounted in the sorption apparatus. This procedure resulted in negligible residual radioactive contamination from one experiment to another.

The simple apparatus for sorption experiments is sketched in Fig. 1. All experiments employed as the aqueous medium 50 or 100 mL of a synthetic groundwater with the concentrations of principal constituents listed in Table 1. In equilibrium with ambient air, the pH was ~7.8 and was largely determined by the equilibrium between CO_2 and HCO_3^- ion. For experiments under anoxic conditions, N_2 gas was bubbled through the solution to remove O_2 and CO_2 . In a typical experiment under anoxic conditions, before the granite specimen was lowered into contact with the solution, the pH attained a steady value of ~9.3.

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Fig. 1. Apparatus for sorption of actinides on rock specimens.

Table 1. Composition of Artificial Groundwater^a (pH = 7.8)

Species	Concentration mg/L	Species	Concentration mg/L
HCO ₃ ⁻	123	Ca ²⁺	18
SO ₄ ²⁻	9.6	Mg ²⁺	4.3
Cl ⁻	70	K ⁺	3.9
SiO ₂ (total)	12	Na ⁺	65

^aReference 2

Radioactive concentrations were chosen to insure adequate deposition on the specimen for an autoradiograph. The nuclides used and their concentrations were: ²³³U, 6.4×10^{-7} M; ²³⁷Np, 4.2×10^{-5} M; ²³⁸Pu, 1.8×10^{-9} M, and ²⁴¹Am, 8.4×10^{-10} M.

In a typical experiment, the apparatus of Fig. 1 was assembled with the granite specimen positioned above the solution until all adjustments were complete and the pH readings attained a constant value. To achieve stable, anoxic conditions required from 5 to 20 hours with the modest flow rates of N₂ gas used here, since it was considered important to avoid premature transfer of solution to the specimen by spattering. The bubbler nozzle was withdrawn from the solution and positioned with the tip a few mm above the surface of the aqueous phase, and N₂ gas flow was maintained at $\sim 0.03 \text{ m}^3 \text{ hr}^{-1}$ during the sorption experiment. The glass rod was adjusted to

immerse the specimen to a depth of 1.5-2.0 mm in the groundwater solution. Typical sorption experiments were carried out for 20-21 hours, unless long-term effects were being investigated. This would yield K_d values approximately 80% of those found for batch equilibrations of 5 days. Other experimental details are given on the captions to the autoradiographs displayed below.

Following a sorption experiment, the specimen was washed with distilled water and dried with tissue. It was then installed in the autoradiograph "camera," whose essentials are shown in Fig. 2. The Polaroid* type 57 4 x 5 sheet film was loaded into a Polaroid* 545 film holder, mounted in the wall of a light-tight metal box containing the other components of Fig. 2. To load the sheet film, the pressure plate was retracted by a lever system actuated from outside. When the envelope was pulled back to uncover the film, the pressure plate was then pressed down so that the radioactive face of the specimen, the ZnS scintillator on mylar film, and the Polaroid film, were all in firm contact. A lever and weight arrangement was employed to provide constant contact pressure during the exposures. The plastic foam pad was found necessary to insure adequate alignment because the specimen was not of precisely uniform thickness.

The high sensitivity of this method for alpha particles arises from the use of the scintillator as a transducer, together with 3000

*Polaroid Corporation, Cambridge, MA 02139.

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Fig. 2. Simplified diagram of autoradiograph camera, showing essential parts..

ASA panchromatic film. The scintillator sheet^{**} is standard silver-activated zinc sulfide [ZnS(Ag)] coated on one side of 0.004-in. (0.1 mm) mylar film. This scintillator film is used extensively in low-level alpha-particle counting. Several other types of Polaroid photographic film were tried, but type 57 yielded by far the best resolution at these light levels. The response of the film appeared to be highly non-linear with respect to time.

The arrangement used in these experiments has proved to be very convenient and reproducible. Duplicate experiments yield qualitatively indistinguishable results. Once the scintillator screen, specimen, and plastic foam pad are attached to the pressure plate with office tape, any desired number of exposures can be made without exposing the scintillator to room light. This is an important advantage, because after exposure to intense room light, about one hour is required for a long-lived phosphorescence in the ZnS(Ag) scintillator to decay to a usable level.

RESULTS AND DISCUSSION

The Climax Stock granite employed in this study is composed primarily of quartz, feldspar, biotite, and pyrite. The mineralogical composition of this granite³ is given in Table 2. In Fig. 3, a reflected light optical photo of the Climax Stock granite, as well as a labelled tracing of the mineral grains, can be seen. In the optical photo the white grains are pyrite (FeS_2), the light grey are

^{**} Available from William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

Fig. 3. Mineralogy of the Climax Stock granite specimen. (a) Optical photograph in reflected light; (b) tracing of (a) coded to identify principal minerals.

Table 2. Composition of Climax Stock Granite^a

<u>Mineral</u>	<u>Chemical Composition</u>	<u>Wt. %</u>
Andesine	$(\text{Na}_{2.3}\text{Ca}_{1.8}\text{K}_{0.01})(\text{Al}_{5.4}\text{Si}_{10.5})\text{O}_{32}$	46%
Quartz	SiO_2	28%
Microcline	$(\text{K}_{3.9})(\text{Al}_{4.1}\text{Si}_{11.97})\text{O}_{32}$	15%
Biotite	$\text{K}_{2.2}(\text{Mg}_{2.61}\text{Fe}_{3.4})(\text{Fe}_{0.7}\text{Al}_{0.45}\text{Ti}_{0.4})$ $(\text{Si}_{5.7}\text{Al}_{2.3})\text{O}_{24}(\text{OH})_2$	10%
Pyrite	FeS_2	1%

^aReference 3.

quartz, the dark grey are feldspars, and the black are biotite. These various components are clearly identified in the tracing. In Fig. 4, a classification of rock types is presented based on mineral composition and grain size. The area that has been shaded fits the mineralogical composition of the Climax Stock best, and since the rock is fairly coarse-grained, it could more appropriately be called a monzonite. The only major deviation mineralogically is the amphibole region, which is almost non-existent in this rock. This granite was chosen specifically for these studies because of its grain size, its reasonably simple, representative mineralogical composition, and its two ferrous minerals.

This granite also exhibited substantial trace impurities of clay minerals that formed from weathering of the feldspars (B. Erdal⁴). These clays appeared to be most abundant along cracks in the granite.

Fig. 4. Classification of rock types according to mineral composition and grain size. The shaded area includes the composition of Climax Stock granite.

The first actinide chosen for study was americium. This choice was due to the fact that the trivalent state is very stable and a large body of data exists for its sorption on pure minerals.^{2,5} In Fig. 5 are given autoradiographs following the sorption of americium on Climax Stock granite under aerated and nitrogen-purged conditions. It appears that slightly reducing conditions do not significantly affect the sorption of the americium. Examining the aerated sorption in more detail one finds that there is general sorption over the whole rock surface, but that the pyrite grains and biotite grains sorb much more strongly; the feldspars exhibit lower sorption; and finally, quartz exhibits almost no sorption. Table 3 contains the distribution coefficients of Am on pyrite, biotite, quartz, and feldspars at a pH of 8.0. The biotite and pyrite are approximately the same, followed by feldspar, and quartz last. Extremely good qualitative agreement between the whole rock and pure mineral measurements is seen. There

Table 3. Distribution Coefficients for Am on Pure Minerals^a

<u>Mineral</u>	<u>Kd(m³/kg) pH = 8.0</u>
Biotite	1.1
Pyrite	0.85
Feldspars	0.3
Quartz	0.1

^aReference 2.

Fig. 5. Sorption of americium from synthetic groundwater. (a) Optical photograph as in Fig. 3(a); (b) autoradiograph after sorption of americium from an aerated solution (exposure 1 min); (c) autoradiograph after sorption of americium from a solution purged with nitrogen (3 min).

appear to be no grain boundary effects at all, but there are some obvious effects from cracks. In the optical photo one can see a large crack running from the pyrite grain in the lower right hand corner of the slab down to the lower edge of the granite; indeed, this can be seen in the autoradiograph. This crack effect may be explained by an observation, mentioned earlier, by workers at Los Alamos Scientific Laboratory⁴ that there are substantial amounts of clay material present in this particular granite due to weathering of the feldspar. This would also correlate well with the sorption isotherms that have been observed for sorption of Am on pure clay minerals.²

The next element of interest is neptunium. In the solutions employed for these studies, the Np is expected to exist as the NpO_2^+ cation. Figure 6 displays the effects of sorption of Np on Climax Stock granite from aerated and nitrogen-purged solutions. A third autoradiograph is shown, from an experiment in which the surface of the granite was oxidized with H_2O_2 prior to exposure to the Np solution. The autoradiograph of this oxidized surface exhibits general sorption across the whole surface that is not specific for any mineral. In contrast, the sorption of Np on the fresh surface of the granite under aerated conditions shows strong sorption of the Np on certain minerals. These minerals turn out to be the Fe(II)-containing minerals pyrite and biotite. There is still some background sorption on the quartz and feldspar, but in contrast to the previously described autoradiograph, the background sorption is much less. The third autoradiograph, from an experiment under nitrogen-purged conditions,

(a) CLIMAX STOCK GRANITE

**(b) Np IN NITROGEN PURGED
SOLUTION**

(c) Np IN AERATED SOLUTION

(d) Np ON OXIDIZED SURFACE

Fig. 6. Sorption of neptunium from synthetic groundwater. (a) Optical photograph of specimen for comparison; (b) autoradiograph after sorption from nitrogen-purged solution (exposure 30 m); (c) autoradiograph after sorption from aerated solution (2h); (d) autoradiograph after sorption from an aerated solution on surface treated previously with H_2O_2 (30 m).

exhibits even stronger sorption on the two minerals pyrite and biotite, and the general background sorption is substantially less. These large changes in sorption as the oxidizing or reducing conditions of the solution change, and the strong correlation of the sorption with the Fe(II)-containing minerals, suggest that the mechanism of sorption most likely involves reduction of NpO_2^+ to the much less soluble Np(IV) by Fe(II).

The third element investigated was uranium, expected to exist in solution primarily as the very soluble cation UO_2^{2+} , which generally exhibits low distribution coefficients for most minerals. Autoradiographs of uranium sorbed on an oxidized granite surface and on an untreated surface from aerated and nitrogen-purged solutions are displayed in Fig. 7. The uranium is not observed to sorb significantly on any of the minerals except biotite. This sorption does not appear to be related to a reduction reaction with Fe(II). This conclusion is supported by two observations. The first is that although the Fe(II)-containing mineral biotite sorbs uranium, pyrite does not; and second, the sorption is not affected by oxidizing or reducing conditions of the solution. The sorption of uranium on biotite appears to be associated with the layered structure of the biotite and its relatively large cation-exchange capacity of 17 mg/kg versus 0.2 mg/kg for quartz. This type of sorption is supported by the fact that when the surface of the granite is polished to remove the uranium sorbed on it, many more treatments are required to remove it completely. Further evidence that this is, indeed, a cation exchange phenomenon is presented in Fig. 8. The ^{233}U was sorbed on the granite in groundwater overnight

(a) CLIMAX STOCK GRANITE

**(b) U IN NITROGEN PURGED
SOLUTION**

(c) U IN AERATED SOLUTION

(d) U ON OXIDIZED SURFACE

Fig. 7. Sorption of uranium from synthetic groundwater. (a) Optical photograph of specimen for comparison; (b) autoradiograph after sorption from a nitrogen-purged solution (exposure, 15 m); (c) autoradiograph after sorption from an aerated solution (15 m); (d) autoradiograph after sorption from an aerated solution on specimen treated previously with H_2O_2 (15 m).

(a) U SORBED IN GROUNDWATER

(b) U SORBED IN 4 M NaCl

Fig. 8. (a) Autoradiograph after sorption of uranium from aerated groundwater; (b) autoradiograph after specimen from (a) was re-immersed in the groundwater which had been adjusted to 4M NaCl. Exposure, 25 m each.

and an autoradiograph taken, then sufficient NaCl was added to the groundwater to make it a 4 M NaCl solution. The granite was re-immersed for a time equal to the previous experiment. As can clearly be seen, the ^{233}U desorbed in qualitative agreement with simple cation exchange behavior.

The last element to be studied was plutonium, which was expected to be predominantly in the tetravalent state and, therefore, quite insoluble. In Fig. 9, autoradiographs are presented for Pu sorbed on the Climax Stock granite from aerated and nitrogen-purged solutions and from a solution of Pu oxidized with O_3 . There appeared to be little effect of aerated or reducing conditions on the sorption. The sorption does exhibit some specificity for the Fe(II) minerals, but the predominant pattern is a general sorption across the entire surface. This is consistent with the behavior that would be expected for PuO_2 , but implies the presence of some PuO_2^{2+} . The sorption from the O_3 -treated solution, in which PuO_2^{2+} should be the predominant species, does exhibit strong correlation with the Fe(II)-containing minerals, implying a reduction mechanism similar to that seen for NpO_2^+ .

CONCLUSIONS

In Fig. 10, the Eh vs pH trends expected⁶ for Pu, Np, and U are presented along with a field showing the range of values of Eh and pH prevalent in deep granitic mines. The autoradiographic experiments are consistent with a range of Eh and pH such that Am should be trivalent; Np should be pentavalent but reduced by Fe(II)-containing minerals; U should be hexavalent; and Pu should be tetravalent, but could be reduced from its hexavalent state by Fe(II)-containing minerals. To satisfy all of these conditions, the Eh and pH region

(a) CLIMAX STOCK GRANITE

(b) Pu OXIDIZED WITH O_3

(c) Pu IN AERATED SOLUTION

**(d) Pu IN NITROGEN PURGED
SOLUTION**

Fig. 9. Sorption of plutonium from synthetic groundwater. (a) Optical photograph of specimen for comparison; (b) autoradiograph of specimen after sorption from a groundwater solution oxidized with O_3 ; (c) autoradiograph after sorption from an aerated solution; (d) autoradiograph after sorption from a nitrogen-purged solution. (All autoradiograph exposures 10 m).

in which these experiments were run would fall at the top of the region observed for granitic mines, as shown by the solid black zone in Fig. 10. Our near-anoxic conditions corresponded to reduction-oxidation potentials in the range of zero to about -0.1 V, while in deep granitic mines, values of potential as low as -0.3 V have been reported.⁷ For such highly negative values of the potential even UO_2^{2+} is reduced to UO_2 , the less mobile form.⁸

It can be concluded from these studies and earlier work on pure minerals² that under aerated granitic groundwater conditions, the prevalent oxidation states in solution for the actinides will be Am(III), Pu(IV), U(VI), and Np(V). Under these conditions an appreciable amount of Np(V) appears to be reduced to Np(IV) by Fe(II)-containing minerals. The predominant oxidation states in solution for nitrogen-purged solutions will be the same as for aerated solutions, but the reduction of Np(V) will be enhanced. These studies and the sorption measurements on pure minerals² indicate that the general order of decreasing sorption will be $\text{Pu(IV)} > \text{Am(III)} > \text{Np(IV)} > \text{Np(V)} > \text{U(VI)}$.

The autoradiographs obtained with Np graphically support the reduction mechanism that was proposed previously¹ for Np and Tc. Further, as mentioned above, the data obtained under nitrogen-purged conditions, which are fairly mild reducing conditions, indicate that under conditions expected in deep geologic formations, even uranium will be reduced to UO_2 , the less mobile form (see Fig. 10).

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Fig. 10. Potential-pH diagram for soluble species of uranium, neptunium, and plutonium. The solid black zone is consistent with the sorption on granite observed here.

The sorption of UO_2^{2+} appears to be the only actinide that exhibits a simple cation exchange mechanism. The sorption of Am(III) and Pu(IV) are dominated by hydrolysis or carbonate complexation reactions.

The sorption of Am derived from the autoradiographs also indicates that the sorption data obtained from batch equilibrations of pure minerals can be used to predict sorption on whole rock samples and that grain boundary and fissure effects are not of sufficient importance to alter the sorption markedly.

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