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MICROAUTORADIOGRAPHY IN STUDIES OF PU(plutonium)(v)
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Author(s):

D. Vaniman, A. Furlano, S. Chipera, J. Thompson,
I. Triay

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MICROAUTORADIOGRAPHY IN STUDIES OF Pu(V) SORPTION BY TRACE AND FRACTURE MINERALS IN TUFF

D. VANIMAN*, A. FURLANO**, S. CHIPERA*, J. THOMPSON**, and I. TRIAY**
*MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545, vaniman@lanl.gov
**MS J514, Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

Microautoradiography was used to evaluate the mineralogic basis of Pu(V) retention by tuffs from Yucca Mountain, Nevada. Altered orthopyroxenes and oxide minerals are associated with high Pu retention, but are limited to specific stratigraphic horizons. A weaker but more general association of Pu with smectite occurs in most samples. Thin-sections that cross fractures allow comparative studies of Pu retention by fracture-lining versus matrix minerals. Using Ag metal in emulsions as a measure of underlying Pu concentration, electron-microprobe (EMP) analysis can quantify Pu retention along fracture walls and provide mineral/mineral Pu retention factors. For smectite-lined microfractures in zeolitized tuff, the smectite/clinoptilolite Pu retention factor is >80 .

INTRODUCTION

Minerals present in trace amounts, if exceptionally sorptive or otherwise retentive of radionuclides, can be significant in retarding radionuclide transport. In order to best understand the mineralogic basis for these processes, it is important to examine interactions with radionuclides on a microscopic scale. To obtain this understanding, optical microautoradiography can be supplemented by electron microprobe (EMP) analysis of Ag in radionuclide-exposed photoemulsions. Ag metal in a developed photoemulsion provides a sensitive measure of the amount of underlying Pu. Alpha decay from Pu generates only a few Ag atoms in the defect-rich AgBr crystals of the radiographic emulsion. However, on development each "latent image" of a few Ag atoms has a higher probability than "unhit" crystals of growing into a ribbon of Ag metal somewhat larger than the original AgBr crystal. These Ag ribbons are a manyfold increase over the original latent signal. When the emulsion is fixed, undeveloped AgBr crystals are removed, leaving only the Ag from the developed crystals; this loss of this other-than-signal Ag is important for EMP analysis, for there is essentially no Ag background contribution from remnant AgBr crystals. Many studies have used this technique to quantify distributions of β -emitting nuclides [1,2,3]. In this paper we use both optical and EMP methods to quantify distributions of α -emitting Pu.

EXPERIMENTAL METHODS

Quantitative X-ray Diffraction (QXRD) and Thin-section Preparation

Splits of the samples used for microautoradiography were analyzed by quantitative X-ray diffraction (QXRD) to determine mineral abundances. The splits were obtained from sample portions adjacent to those used for thin-section preparation. A Siemens D-500 diffractometer was used, employing Cu-K α radiation and a Kevex Psi Si(Li) solid state detector. A split of each sample was mixed with a 1.0- μ m corundum internal standard in a sample:corundum ratio of 8:2 by weight. The quantitative mineralogy was determined by matrix-flushing methods[4].

Serial thin-sections were prepared to provide an untreated thin section for petrographic analysis and several parallel sections for microautoradiography. Thin-

section preparation methods using alcohol and water, kerosene and water, and water only were tested to determine whether these various fluids had any effect on Pu retention, particularly in smectite-rich samples; it was found that these variations in fluid exposure had no effect on microautoradiography results. In early experiments, rock slices separated from their glass slides when immersed in Pu solution. These samples could still be studied by optical microautoradiography methods, but could not be used for EMP analysis of Ag in the developed emulsion. For sample 1244, thin-section mounting with UV-setting epoxy was used to prevent separation of the rock slices from the thin-section glass.

Exposure to Pu(V) Solution

The ^{239}Pu solution was prepared by adding an aliquot of well-characterized Pu(V) acidic stock to Na-bicarbonate water to obtain a Pu concentration of 10^{-6} M, just below saturation for Pu-carbonate. The water used was a Na-bicarbonate buffer (simulating the water chemistry of well UE-25p#1 at Yucca Mountain). The synthetic UE-25p#1 water was prepared by dissolving 0.39 g of Na_2CO_3 and 8.90 g of NaHCO_3 in 10 l of deionized (DI) water. Solutions used to immerse thin sections were analyzed by pulsed-laser photoacoustic spectroscopy to confirm that the Pu species in solution was Pu(V).

Several methods of contacting Pu solution with thin sections were tested. Initially, thin sections were placed on top of a wet towel inside a petri dish, the thin section was wetted with a thin film (300 μl) of the ^{239}Pu solution, and the petri dish was sealed overnight. On two of the sections, however, the Pu solution evaporated; it is unknown to what extent the others so treated may have experienced evaporative concentration of the Pu solution. To obtain results without evaporation, all other thin sections were immersed in a larger volume (20 ml) of Pu solution. The three different results are here referred to by the terms *thin film*, *evaporated*, and *immersed*.

After thin sections were removed from Pu solution, they were rinsed with DI water. The radioactivity in each thin section was measured with a Methane Flow Proportional Counter (MFPC). Each thin section was then immersed in a solution containing 4 g of

Fig. 1: (a) Example of a stellate ^{239}Pu α -decay track cluster on quartz microphenocryst (devitrified Prow Pass Tuff, 1165,T3; 50 μm scale bar). (b) Example of a uniform ^{239}Pu α -decay track cluster. Track abundances in the upper right are greater than the "background" track abundances to the left. The abundant tracks overlie a smectite-bearing portion of the sample (zeolitized Calico Hills Formation, 1161,T4; 50 μm scale bar).

parlodion in 200 ml of methyl alcohol and 200 ml of ethyl ether, which prevents further contact with water. Each section was then dried and counted again. A thin layer prepared with 2 g of gelatin and 0.25 g of $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 400 ml of DI water was applied to each section and dried. A Kodak radiography emulsion was then mounted on the thin sections in a darkroom, under red safelights, by contacting each section with the surface of the emulsion. Each thin section was then placed in a light-tight box and exposed until about $10^6 \alpha$ disintegrations/cm² were accumulated, based on the α activity measured with the MFPC. After exposure, the emulsion in contact with each sample was developed and fixed using Kodak D-19 developer and Kodak fixer.

Optical Analysis of Thin Sections

Petrographic analysis was used to characterize minor and trace minerals in standard thin sections. Analysis of developed ²³⁹Pu decay tracks in microautoradiography sections was done at magnifications up to 500x. Rock slices that separated from the glass slides during exposure to solutions were coated with immersion oil and pressed to a clean slide under cover glasses for optical examination. There are two modes in which enhanced track concentrations appear: (1) clusters of tracks that radiate from point sources (*stellate* track clusters, Fig. 1a) and (2) tracks dispersed evenly across specific petrologic features (*uniform* track clusters, Fig. 1b). Individual tracks were not counted. Instead, either the individual stellate clusters were counted or, where the track concentrations were uniform, each group of tracks equal in number to a typical stellate cluster was counted.

Electron Microprobe (EMP) Analysis of Developed Emulsions

Measurements of Ag in emulsion were obtained with a Cameca SX-50 electron microprobe (accelerating potential 15 keV, beam current 15 na, spot size of 10 μm). Ag L-line emission was peaked on a PET crystal using pure Ag metal. A representative coating of the radiographic emulsion on a glass slide, exposed to full sunlight for saturation, developed, and fixed, was also examined to evaluate the Ag signal of a saturated emulsion. Backgrounds for both the Ag metal and the saturated emulsion were obtained at ± 0.01200 sine Θ . Count rates on pure Ag metal were $53,100 \pm 250$ per 15 sec on five spots; background counts calculated for the peak position (assuming linear background) were 280 per 15 sec, averaged from high and low background counts. Count rates on the saturated emulsion were $32,600 \pm 530$ per 15 sec on 20 spots; background counts at the peak position (assuming linear background) were 210 per 15 sec, averaged from high and low background counts. In analysis of actual samples, linescans were collected across selected locations on the developed emulsion surfaces of Pu-exposed thin sections. The dwell time per spot in each linescan was 15 sec, with a 12- μm spacing between spots along the line of scan.

CHARACTERIZATION OF STARTING MATERIALS

Petrographic and QXRD analysis of the starting materials provide an inventory of the phases available for interaction with the Pu solution. Table I summarizes the variety of trace phases in these samples; Table II lists the QXRD-determined abundances of major and minor phases. The samples used are a representative variety of tuff lithologies: Densely-welded devitrified, poorly-welded devitrified, nonwelded vitric, and nonwelded zeolitic tuffs.

The densely-welded devitrified sample, from the upper Topopah Spring Tuff (sample 587, 130 m depth, core USW G-1), is a fine- to medium-grained tuff with granophyric texture. Spinels (magnetite/maghemite, <200 μm) have limited alteration; biotites (~0.4

Table I: Trace Phases of Potential Significance in Autoradiography/Sorption Samples

	587 Topopah <i>devit</i>	1161 Calico <i>zeol</i>	1162 Prow Pass <i>zeol</i>	1164 Calico <i>vitric</i>	1165 Prow Pass <i>devit</i>	1244 Calico <i>zeol</i>
spinel	x	x	x	x		+
spinel corona						
hematite	x			x	x	+
hydrous oxides		x				
biotite	x	x	+	x	x	x
amphibole				x	+	
clinopyroxene				x		
orthopyroxene			+	x	x	
zircon	+		+	+	+	+
apatite	+			+	+	
allanite?	+					
calcite	x			x		

Magnetite/maghemite listed as spinel; abbreviations used for devitrified (devit) and zeolitic (zeol). Presence in sample in amounts close enough to 1% to be readily evaluated by autoradiography is indicated by x; presence in amounts <<1% is indicated by +.

Table II: Mineral Percentages in Autoradiography/Sorption Samples, Determined by QXRD

	587 Topopah <i>devit</i>	1161 Calico <i>zeol</i>	1162 Prow Pass <i>zeol</i>	1164 Calico <i>vitric</i>	1165 Prow Pass <i>devit</i>	1244 Calico <i>zeol</i>
smectite	2(1)	2(1)	1(1)	4(1)	1(1)	9(3)
mica	tr	-	-	1(1)	tr	-
amphibole	-	-	-	tr	-	-
clinoptilolite	-	62(8)	52(9)	4(1)	-	58(6)
mordenite	-	11(4)	24(8)	-	-	5(2)
tridymite	18(3)	-	-	-	-	-
quartz	1(1)	3(1)	2(1)	11(1)	9(1)	5(1)
cristobalite	6(3)	-	-	2(1)	24(2)	-
opal-CT	-	19(5)	1(1)	-	-	20(5)
feldspar	72(15)	8(2)	22(7)	26(4)	62(9)	10(2)
calcite	tr	-	-	1(1)	-	-
glass	-	-	-	50(5)	-	-
hematite	1(1)	-	-	1(1)	tr	-

Values in weight percent, errors in parentheses approximately two standard deviations. Abbreviations used for devitrified (devit) and zeolitic (zeol). Dashes (-) indicate phase not detected in XRD; "tr" indicates detection in trace amounts (<0.5%). Data for sample 587=av. of two bracketing samples.

mm) are extensively altered and oxidized. The edge of this sample has a fracture face lined by a thick deposit of calcite+opal; these phases showed essentially no retention of Pu in microautoradiography and the data for this sample in Tables I-III are only for the devitrified tuff. The poorly-welded devitrified sample, from the Prow Pass Tuff (sample 1165, 532 m depth, core USW GU-3), contains highly altered and oxidized microphenocrysts of biotite (≤ 1 mm), orthopyroxene (~ 0.2 mm), and smaller amphibole (< 10 μ m). Small grains of hematite (~ 20 μ m) are scattered throughout the groundmass.

A nonwelded vitric sample from the Calico Hills Formation (sample 1164, 469 m depth, core USW GU-3) contains abundant crystals and glass pyroclasts of ~ 0.25 mm that are relatively unaltered. Hematites and oxidized magnetite/maghemite are smaller (50-100 μ m). Small amounts of calcite occur in pore spaces; minor clinoptilolite may be both allogenic and authigenic.

Three zeolitic samples were studied, one from the Prow Pass Tuff (sample 1162, 629 m depth, core USW G-4) and two from the Calico Hills Formation (sample 1161, 509 m depth, core USW G-4 and sample 1244, 396 m depth, core UE-25 UZ#16). These samples have varying ratios of clinoptilolite and mordenite as well as varying amounts of lithic fragments and of quartz and feldspar phenocrysts. The sample from the Prow Pass Tuff (1162) has very little opal-CT intergrown with its zeolites and has well-preserved shard textures. The samples from the Calico Hills Formation (1161, 1244) have more opal-CT; sample 1244 has a brecciated fabric with smectite-lined microfractures, leading to the high smectite abundance (9%) noted in Table II.

RESULTS OF MICROAUTORADIOGRAPHY

Optical Analysis

Results of optical counting of track concentrations are summarized in Table III. The thin-film and evaporated sections generally have abundant stellate clusters of Pu decay tracks. Such clusters are less common in the immersed sections. This difference indicates that evaporative concentration of the solution is an important factor in generating point concentrations of Pu, leading to some stellate clusters. Evidence of this is seen in the common occurrence of stellate clusters on mineral grains in which strong sorption should not occur (e.g., quartz phenocrysts). This does not necessarily mean that precipitation alone accounts for the stellate clusters; some sorption is likely to occur before Pu concentrations rise to the point of Pu precipitation.

While it is useful to compare track concentrations in different regions of the same thin section, it is not valid to compare different thin sections to each other. There are many reasons - in addition to sorption properties - why different thin sections can have different track densities. Differences in conditions of exposure to the solution, in effectiveness of rinsing after exposure, in effectiveness of emulsion coating, and in times of development are factors that can lead to significant differences in apparent track densities between thin sections. Although the percentages of track concentrations on different features vary between the immersed and other samples (thin-film or evaporated), the same features stand out in all treatments. In sample 1162 (zeolitized Prow Pass Tuff), smectite is the predominant Pu-retaining mineral in both immersed and evaporated samples. The same is true in sample 1164 (vitric Calico Hills Formation). However, the percentages of "spurious" track concentrations (e.g., track concentrations on quartz, feldspars, and glass pyroclasts) is much higher (13% to 60%) in the evaporated samples than in the immersed samples (0% to 7%). The thin-film experiment with sample 1165 (devitrified Prow Pass Tuff) also has a fairly high abundance of "spurious" tracks (9%). These results show that more reliable results are obtained with the immersion method.

Table III: Track-Cluster Associations in Six Tuff Samples

	devit. Topopah Spring	zeolitic Calico Hills	zeolitic Prow Pass	zeolitic Prow Pass	vitric Calico Hills	vitric Calico Hills	devit. Prow Pass	zeolitic Calico Hills
<i>feature:</i>	587,t1 Im.	1161,t4 T.F.	1162,t4 Ev.	1162,t5 Im.	1164,t3 Ev.	1164,t5 Im.	1165,t3 T.F.	1244,t1 Im.
smectite	32%?	60%	59%	75%	35%	86%	18%	81%
*FQCT	?%	4%	n/a	n/a	1%	1%	54%	6%
glass	n/a	n/a	n/a	n/a	41%	4%	n/a	n/a
zeolite	n/a	32%	5%	21%	0	0	n/a	9%
K-feldspar	2%	1%	5%	1%	5%	1%	3%	0
plagioclase	0	0	5%	0	9%	1%	2%	0
quartz	1%	0	3%	0	5%	1%	4%	0
biotite	1%	0	23%	3%	4%	1%	1%	2%
amphibole	n/a	n/a	n/a	n/a	0	2%	0	n/a
pyroxene	n/a	n/a	0	0	0	2%	12%	n/a
oxides	60%	3%	0	0	0	0	1%	2%
calcite	4%	n/a	n/a	n/a	0	1%	n/a	n/a
allanite	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
mudstone	n/a	n/a	n/a	n/a	n/a	n/a	5%	n/a
#of track clusters	136	132	39	97	190	162	827	178

"Im."=immersed, "T.F."=thin film, "Ev."=evaporated (see *Experimental Methods*);
 "?" indicates difficulty in resolving finely-intergrown smectites and welded
 groundmass. *FQCT=fine-grained feldspar $\pm$ quartz $\pm$ cristobalite $\pm$ tridymite.

For both the zeolitic Prow Pass Tuff (1162) and the vitric Calico Hills Formation (1164), more tracks are associated with smectite in immersed than in evaporated samples. This could be the result of higher water-to-smectite ratios in the immersed samples, leading to swelling of the smectite and greater exposure of smectite interlayers where charged complexes can be affixed. However, examination of smectites in thin section shows that they are kept from expanding by epoxy introduced during thin-section preparation. Alternatively, Pu may precipitate at random in evaporated samples, reducing the amount of Pu that might otherwise be affixed to smectites if evaporative concentration did not occur. We consider this to be the principal cause of decreased Pu/smectite associations in evaporated samples, because the percentages of Pu track correlations with features that should not be sorptive (glass, quartz, and feldspars) in the evaporated samples would, if reallocated to smectites, come very close to the Pu/smectite correlation percentages in the immersed samples.

Electron Microprobe (EMP) Analysis

Figure 2 shows an EMP linescan collected across a smectite-rich fracture lining in zeolitic sample 1244. The raw counts for Ag are represented for each point along the linescan, with each point representing a step where the electron beam was allowed to rest for 15 sec while Ag counts were accumulated. The walls of the fracture, lined by smectites, are clearly marked by high Ag concentrations corresponding to exceptionally high Pu retention. The zeolitic tuff that forms the matrix away from the fracture walls has Ag counts per 15 sec that are only marginally higher than background (av. 360 ± 90 counts per 15 sec, determined from 25 analytical points on zeolitic tuff; in comparison, the instrumental background in the emulsion is 210 counts per 15 sec).

Fig. 2: Electron microprobe linescan for Ag across a fracture with smectite-lined walls; matrix on either side is zeolitic (sample 1244). Open fracture is approximately at point 33 (10 μ m beam, 15 sec/point).

CONCLUSIONS

Identification of Exceptionally Sorptive Phases

The distributions of ^{239}Pu α -decay tracks in all of the samples studied indicate only three definitive mineral associations that have appreciably enhanced affinity for Pu. Two of these associations are very restricted in occurrence: the altered orthopyroxenes of the devitrified Prow Pass Tuff (sample 1165) and the altered opaque oxides of the upper Topopah Spring Tuff (sample 587). The third association, however, is with smectites that are much more widely distributed.

Although orthopyroxene microphenocrysts account for less than 1% of the devitrified Prow Pass Tuff, they hold 11% of the Pu track concentrations in this sample (sample 1165). It is evident that it is the alteration features specific to the orthopyroxenes, rather than the unaltered pyroxene, that retain Pu. Further evidence of the importance of alteration is found in sample 1164, of the vitric Calico Hills Formation, in which the unaltered orthopyroxenes do not accumulate Pu. Moreover, it appears that a specific type of orthopyroxene alteration is necessary to attract Pu; the altered orthopyroxenes of the zeolitic Prow Pass Tuff (sample 1162) do not accumulate Pu, whereas the altered orthopyroxenes of the devitrified Prow Pass Tuff do (sample 1165). XRD analysis of separated grains from sample 1165 show that the altered orthopyroxene consists of amphibole and Fe-rich amorphous material.

In sample 587, from the upper part of the rhyolitic devitrified Topopah Spring Tuff, the oxide minerals account for less than 1% of the tuff but hold 60% of the Pu track concentrations. As with the altered orthopyroxenes in sample 1165, the oxide minerals that retain Pu have stellate clusters that are concentrated around the mineral edges and

along internal fractures (distributions of tracks along fractures within these opaque grains can be seen in reflected light, through the film coating).

The Pu associations with smectite are much more significant, because smectites are widely distributed. XRD and scanning electron microscopy of many samples show that the smectites are Fe-rich. These smectites are common products of some of the latest alteration at Yucca Mountain and are therefore distributed in fractures and porous intervals where passage of water has occurred in the recent past and is likely to be channeled in the future. Although smectite accounts for at most 9% of the samples studied, the smectites hold 18% to 86% of the Pu track concentrations, providing a common and effective barrier to Pu transport.

Quantification of Mineral/Mineral Pu Retention Ratios

The analysis of developed radiographic films by EMP provides a means of quantifying mineral/mineral radionuclide retention ratios. However, certain caveats must be considered when using this technique. First, the use of planar thin sections provides a 2D view of what is essentially a 3D process. This should be a minor problem; all phases are still represented, although the matrix minerals are more exposed in a thin section than they would be in a bulk sample. Second, Ag contents in emulsions are variable and the emulsion itself can be somewhat irregular in thickness, surface texture, and distribution of α -track "noise." The variability in emulsion and in random α -track occurrences is nevertheless a minor problem if Ag abundances are compared between immediately adjacent mineral grains, on a scale where the emulsion coverage and properties are uniform. Third, the size of the electron beam (in this study, 10 μm) may be larger than the individual minerals of interest. The smectite bodies analyzed in thin section 1244 are aggregates that are $<10\mu\text{m}$ wide; where smectite bodies are wider, they are generally interspersed with either zeolites or epoxy. The maximum count rates for Ag obtained over smectite (about 12,600 background-corrected counts per 15 sec; Fig. 2) are probably less than would be obtained from an absolutely pure smectite, without epoxy impregnation, exposed to the same Pu solution. For the data obtained in this study by EMP, the calculated smectite/zeolite distribution factor is:

$$(\text{maximum background-corrected counts for smectite})/(\text{background-corrected counts for clinoptilolite}) = 12,600/150 = 84$$

The 2D vs. 3D exposure geometry should not affect this ratio; however, the effect of EMP beam size compared to the smaller sizes of smectite bodies will make this apparent smectite/clinoptilolite Pu retention ratio smaller than the true ratio. Thus the true smectite/clinoptilolite Pu retention factor is greater than indicated above and may best be described as being >80 .

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