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GEOCHEMICAL DISPERSION OF URANIUM NEAR PROSPECTS IN PENNSYLVANIA

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ABSTRACT

The geochemical dispersion of uranium has been investigated near sedimentary uranium prospects in eastern and north-central Pennsylvania.

Near Jim Thorpe, known uranium occurrences in the Catskill Fm. are limited to the base of the Duncannon member. At Penn Haven Junction, roll-type U deposits with appreciable Pb and Se are localized adjacent to an oxidized tongue of channel-filling conglomeratic sandstone. The channel and encircling U occurrences furnish a large target for geochemical exploration.

Selective extractions show that the organic, Fe-oxide, sand and silt fractions of stream sediments are the major hosts for U in stream sediments. Fe-oxides have a greater affinity for U than organic matter but are less abundant. The U content of organic matter is about 10^5 x the U content of stream water.

Stream sediments furnish a representative sample of the average content of U, Zn, Cu, and major elements in soils of a drainage basin in north-central Pennsylvania, so a semiquantitative appraisal of weathering uranium occurrences can be made from stream sediments in climates and topography like Pennsylvania. The flux of uranium leaving the basin in solution is about equal to that leaving as sediment. Uranium is considerably less mobile than Ca and Na.

A new method of extracting uranium from water samples, using a liquid ion exchanger (Amberlite LA-1), shows promise for simple field application.

CONTRIBUTORS

Parts of the research reported, mainly dealing with improved methods of uranium concentration and analysis, were carried out by M. L. Keith and by C. K. Hsi, under Dr. Keith's supervision. Technical assistance in uranium analysis by the delayed neutron method was provided by W. A. Jester of the Nuclear Engineering Department and by the staff of the Breazeale Nuclear Reactor, including I. B. McMaster, D. C. Raupach, R. E. Totenbier, and D. S. Vonada.

INTRODUCTION

Planning and interpretation of geochemical surveys require a knowledge of the chemical and physical processes dispersing elements away from ore bodies. In the case of uranium, relatively little detailed information on its mode of dispersion has been published. In this project, we have examined the processes responsible for dispersion of U near uranium prospects in northeastern and north-central Pennsylvania. These localities appear to be the most nearly economic prospects in eastern United States. At one locality in this area, a small amount of uranium ore was mined and sold to A.E.C. in the 1950's.

Three aspects of uranium dispersion have been studied. First, the distribution of U and other elements in sandstones in and near the Penn Haven Jct. prospect along the Lehigh River in Carbon County, Pa., has been investigated. In conjunction with mapping the exposures, the "ore zone" was found to be a roll-like body located immediately adjacent to an Fe-stained conglomeratic sandstone lens that probably had better permeability than the surrounding sandstones. Outside the U roll and channel, the sandstones are less permeable and are chemically reduced. A close similarity to Wyoming-type deposits is evident. The distribution of traces of U, as well as the best mineralized zone, also appears to be related to this permeable sandstone.

Second, the form in which uranium and other elements occur in stream sediments of the area has been investigated by selective chemical treatments of samples. Methods of selectively dissolving or separating organic matter, Fe oxides, Mn oxides, clays, and other fractions were developed, as well as a new technique for chemically analyzing the fractions for uranium.

Third, the content of uranium in stream sediment has been compared with the average content of uranium in soils and rocks of a small drainage basin to determine whether stream sediments are representative of their drainage basins. The amount of U transported out of the basin in solution and in suspension has been measured and compared with the proportion transported in bottom sediment.

In addition to studies of uranium dispersion, experiments in determination of uranium in various types of samples have been made, using a liquid ion exchanger (Rohm and Haas Amberlite LA-1), an organic extractant (tri-n-butyl phosphate, TBP), ion exchange resins, and the fission track method. The results of work with the liquid ion exchanger and TBP are reported here. The liquid ion exchanger appears suitable for field use in concentrating uranium from natural waters for later analysis by neutron activation or fluorimetry. TBP was successfully used for analysis of uranium in a variety of aqueous solutions used for selective leaching of stream sediment samples. Ion exchange resins are reported on by Korner and Rose (1977). The fission track results will be reported on in a later report by Langmuir and others dealing with studies of ground water.

GEOLOGICAL AND GEOCHEMICAL STUDIES NEAR PENN HAVEN JUNCTION

Geology of the Penn Haven Junction Area

The geology and distribution of uranium occurrences in the Jim Thorpe area, Carbon County, Pa., are illustrated in Figure 1. Most of the U occurs in the Catskill Formation, a 7800'-thick sequence of fluviatile red to gray shale, sandstone, and local conglomerate of upper Devonian age. Other stratigraphic units in the area are summarized in Figure 2. Uranium also occurs just NW of Jim Thorpe in conglomeratic sandstone transitional between red-beds of the Mississippian Mauch Chunk Fm. and sandstones of the Pennsylvanian Pottsville Fm.

Folding in late Paleozoic along axes trending about N80E produced very tight folds and local complex faulting in the anthracite coal district just to the west of the area, but these folds die out rapidly eastward into the gently folded Pocono plateau on the east. Recrystallization has reduced the porosity and permeability of the sandstones to essentially zero, and has produced a cleavage in some shale units on the limbs of folds.

Regional studies of the Upper Devonian, which in the Jim Thorpe area is composed mainly of the Catskill Formation, show it to have enormous extent and thickness. The overall geometry of the Upper Devonian and the Catskill Formation is that of a westward-thinning clastic wedge, truncated by erosion on the eastern edge where the Upper Devonian reaches a maximum thickness of 9,400 feet (Ayrton, 1963). Jim Thorpe is about 7 miles west of the truncated edge, near Lehighton. Paleodirectional indicators demonstrate northwest dispersal trends throughout the Catskill and the probability of an eastern source (Burtner, 1963; Epstein et al., 1974). General trends in the lithofacies from sandstones in eastern Pennsylvania and New York to shales in

Figure 1. Geology and uranium occurrences near Jim Thorpe, Pennsylvania. Shaded area is outcrop of Duncannon Member of Catskill Fm. X = uranium occurrence. Box indicates area of Figure 3. Geology after Sevon (1975).

western Pennsylvania and eastern Ohio also support this overall genetic concept of the Upper Devonian. The source regions were probably in the Piedmont area a few tens of miles to the southeast, where a variety of meta-sediments and igneous rocks are now exposed.

Within the Catskill Formation, low rank graywackes are dominant, but a wide variety of lithofacies are present, ranging from shales and siltstones to very coarse conglomeratic sandstones and in color from grays and greens to very conspicuous dark red. The systematic but complex variations in lithology, along with those of primary structures, have been used by Epstein et al. (1974) to subdivide the formation into nine members (Figure 2).

Figure 2 also shows the lithologic characteristics of the Catskill members and the depositional environments as interpreted by Epstein et al., together representing stages in the development of a prograding delta complex and alluvial plain (Glaeser, 1974). The lower 4,165 feet represent prodelta, delta front, and delta plain environments, while the upper 3,699 feet are attributed to braided and meandering streams.

The upper half of the Catskill differs from the lower half in grain size, bed form, and bed sequence within cycles. Together the Packerton, Sawmill Run, Berry Run, and Clark's Ferry members may be viewed as a coarsening-upward sequence, with increasing proportions of conglomerate and a predominantly gray-green color, reflecting reduced iron. Grain sizes range from those of fine and very fine grained sandstones with minor shale and siltstone in the Sawmill Run and Packerton members to coarse and very coarse grained sandstones and conglomerates with cobbles as large as six inches in the Clark's Ferry member. Throughout all five members, crossbedding is common, but a notable, repeating three-component sequence of steeply downstream-

Figure 2. Stratigraphic section of the Catskill Fm. between Jim Thorpe and Lehigh, Pa., after Epstein et al. (1974).

dipping and shallow, upstream-dipping crossbeds along with intervening parallel beds is characteristic of only the four lower members. These bed forms have been interpreted as the products of migrating sand dunes during normal and flood stages of a large braided stream. The lack of fine grained detritus is interpreted as an indication of the constancy of bed load transport. An excellent discussion of these conclusions is given in Epstein et al. (1974).

The Duncannon member, which is set apart from the four underlying members by virtue of its shale and siltstone content, is also distinguished by its prominent fining-upward cycles and the abundance of red coloration which is uncommon in the underlying four members. Red conglomeratic sandstone, which is not present anywhere else in the Catskill Formation, forms the base of several of the fining-upward cycles. Above the conglomerate, the cycles contain fining-upward sequences of sandstone and, when complete, are capped by shale and siltstone, nearly all of which is red. Sandstones range in color from green and gray to various shades of red, red sandstone being rare elsewhere in the Catskill Formation with the exception of the Long Run member. Twelve of these cycles were observed by Epstein et al. in the Duncannon reference section and strongly resemble those described by Allen (1964) as the standard fluviatile cyclothem. Along with the basic characteristics of the cycles, crossbedding in the basal conglomerate and the desiccation features of the shales and siltstones indicate an origin on an alluvial plain and have been suggested as the product of meandering streams (Epstein et al., 1974).

Distribution of Uranium Near Penn Haven Junction

Figure 3 shows the location of all currently known uranium concentrations in the Penn Haven Jct. area, using a radioactivity of 3x background

as a threshold. Two clusters of occurrences are apparent, one in the vicinity of Icebox Creek and the other near Tank Hollow. At least three of the occurrences on the west side of the Lehigh have mirror images on the east side, located across the river along lines parallel to the structural axes. This symmetry was previously recognized (Klemic et al., 1963), and numerous additional concentrations found during this study have emphasized the same pattern. More occurrences, further defining this symmetry, probably exist south of Butcher Hollow on the east side of the Lehigh River, but poor outcrop prevents finding them.

Each of the two clusters of occurrences is located in sandstone (presumably the upper Clark's Ferry - see next section) near the axis of a minor anticline. This unit is covered in the intervening synclinal fold. Consequently, any uranium concentrations located at this horizon are exposed only along the anticlinal crest, resulting in the apparent clustering. This effect is more clearly seen on the cross section (Figure 3).

In order to define the structure as shown on Figure 3, identifiable units demonstrating reasonable continuity were mapped. The sandstone units of the Duncannon were too variable and discontinuous for this purpose; however, three red shale and siltstone units were usable. These units represent the tops of at least three upward-fining cycles and can be traced sufficiently well to define the folds.

A better control was needed to define the structure in the immediate vicinity of the fold axis at Icebox Creek for the purpose of more detailed work. The top of the conglomeratic sandstone, presumably the basal Duncannon (see next section), was selected as the control horizon because of its prominent topographic expression and close stratigraphic proximity to the

7.

uranium concentrations. By using tape and compass techniques, the top of this unit was shown to conform to the overall anticlinal pattern revealed by tracing the red shale and siltstone units. Its base and consequently its thickness were found to be very variable over the full extent of its exposure.

Stratigraphic Position of Uranium near Penn Haven Junction

The position of the uranium concentrations within the established stratigraphic framework of the Catskill Formation is important for determining possible sedimentary or tectonic controls for the uranium mineralization, as well as local continuity between outcrops. Previous mapping in the area (Sevon, 1975) indicated that the host rocks for uranium in the Lehigh River gorge south of Penn Haven Junction are within the Duncannon member, and that no lower units are exposed. A detailed measurement of the exposed section and a comparison with the stratigraphic section at Jim Thorpe were made to determine the position of the mineralization within the Catskill and the exposed Duncannon member.

Direct correlation between the reference section and the Penn Haven Junction section is hindered by the extreme lateral variability of the lithologies and apparent rapid changes in the thickness of the members. As described in the reference section (Epstein et al., 1974), the base of the Duncannon is a "commonly red conglomeratic sandstone containing eroded and incorporated chips of the underlying siltstone or shale." The underlying Clark's Ferry member is greatly different from the Duncannon when considered as a whole, but individual beds can be quite similar to some in the Duncannon. Consequently, without having at least 100 feet of exposed rock beneath this siltstone unit to confirm the dominant non-red color of the

Clark's Ferry member, an assessment of the stratigraphic position of the mineralization, based strictly on lithology, can only be considered as an approximation.

The reported thickness of the Duncannon in the reference section is 968 feet (Epstein et al., 1974), but the mapped position of the contacts suggests a maximum of 700 ft. The total exposed Duncannon in the Penn Haven Junction section, measuring down from the distinctive Spechty Kopf Fm., is about 750 feet. Lithologically, they resemble each other in the percentages of the various rock types and the percentage of red color within each lithology. Of particular interest is the similarity between the lowest unit shown on the Penn Haven Junction column and the base of the Duncannon in the reference section at Jim Thorpe. The similarities suggest that the majority of the Duncannon may be exposed in the Penn Haven Junction section.

Therefore, it is tentatively concluded that the lowermost conglomeratic, reddish sandstone exposed south of Penn Haven Junction represents the basal unit of the Duncannon member, and that beds below that horizon probably belong to the Clark's Ferry member. Since all of the uranium occurrences so far found south of Penn Haven Junction are located beneath the same conglomerate (with the exception of those in Tank Hollow, which occur immediately above the conglomerate), it is also concluded that they are within the Clark's Ferry member.

Even if the above conclusion is incorrect, the uranium occurrences in the vicinity of Penn Haven Junction clearly lie very close to the base of the Duncannon. Epstein et al. (1974) and the present study showed that the uranium occurrences in the reference section at Packerton Junction south of

Jim Thorpe are located both in the lower Duncannon and the uppermost Clark's Ferry member of the Catskill. In addition, most occurrences in the Clark's Ferry railroad cut at Packerton Junction are just below the basal conglomeratic sandstone of the Duncannon, much like those at Penn Haven Junction.

The possibility of uranium occurrences higher in the section than those already known south of Penn Haven Junction is largely undetermined. Dense vegetation and sparse outcrops have limited direct search by scintillation counter to the railroad cuts and exposures along noses and tributaries to the Lehigh River. All uranium located in this way was within the limits already described. However, stream sediments collected at the first fork of Tank Hollow at a distance of over 2,000 feet from the Lehigh River and an elevation over 200 feet above the presumed base of the Duncannon did show a persistent anomaly in uranium, suggesting occurrences higher in the section (Rose et al., 1976). Although no direct evidence for these anomalies was found in upstream outcrops, the outcrops are sparse and relatively weathered.

Relation of Uranium Concentrations to Host Rocks

Because of the subtle and gradational changes in most aspects of the host rock associated with the uranium concentrations, a scaled diagram of the railroad cut was prepared from overlapping photographs of the exposures, and details of grain size, color changes, bedding features, and mineralization recorded thereon (Plate 1).

The first important fact revealed by diagraming of the outcrop was the lens or channel-like shape of the conglomeratic sandstone overlying the uranium concentrations. The thickness varies from less than 5 feet on the

north end of the section to over 25 feet at the south end. A further increase in thickness was observed before the outcrop ends approximately 1000 feet to the south. Although the base of this conglomeratic sandstone is gradational over several inches and only locally shows an erosional unconformity, the base, as shown on Plate 1, was easily determined and represents the lower limit of quartz pebbles. Quartz pebble distribution within the unit is highly irregular, with the greatest concentration found in scour channels.

Shapes of the uranium concentrations vary from the distinctive "C" shape, which contains both concordant and discordant parts, to elongate pods sub-parallel to bedding, to essentially equidimensional pods bearing no relation to bedding. When all the individual concentrations are considered together, they define a narrow zone, several feet thick, extending over 400 feet, which is roughly parallel to the base of the conglomeratic sandstone. The greatest concentration of uranium within this zone is near the discordant part of the "C," with uranium values decreasing and the pods becoming smaller and less continuous beneath the thicker portions of the conglomerate.

Both red and gray-green colorations, as well as intermediate and transitional colors, are present in the sandstone beneath the conglomeratic sandstone (see Plate 1), but careful sampling and sketching were necessary to reveal any consistent pattern. The conglomeratic sandstone unit is characterized by a dominantly tan or pinkish overall color, defined by sparse hematitic staining and granules, but its very coarse grain size and irregular distribution of white quartz pebbles and green chloritic clasts prevented

accurate color determinations. Therefore, the work on pigmentation presented here is restricted to the underlying sandstone hosting the uranium concentrations.

The boundary shown on Plate 1, between obviously red and obviously non-red rocks in the outcrop, was sharply defined throughout the section except in the vicinity of the "C-roll," where it was gradational and irregular. The boundary is only locally concordant with bedding or influenced by grain size, but it is roughly parallel to the base of the conglomeratic sandstone. A consistent 20-25 foot thickness also characterizes the zone of red coloration except in the vicinity of the "C-roll" where it thins and terminates in a lobate configuration.

The uranium concentrations bear a striking spatial resemblance to the interface between red and non-red rocks. A close parallelism exists between the zone of uranium mineralization and the color boundary throughout the entire section. This is especially conspicuous in the vicinity of the "C-roll" where the discordant part of that concentration closely resembles the lobate end of the zone of red coloration. Similar relations were noted throughout the area south of Penn Haven Junction, with the uranium being restricted to gray-green rocks in close proximity to zones of red coloration.

Occurrences located directly across the Lehigh River from those shown in section A-A' on Figure 3 are almost identical to those already described in previous sections, except that they are more extensive. An en echelon set of three "C-rolls" exists on the East side of the Lehigh (see Figure 4), producing a nearly continuous mineralized zone over 250 feet long (see Klemic et al., 1963) with sporadic extensions over another 100 foot

Figure 4. Uranium occurrences on east side of Lehigh River (after Klemic et al., 1954). Shown are prominent bedding and cross-bedding features. Outline of uranium-enriched zones is drawn at ≈ 800 cps. Zones of maximum radiation are indicated with vertical line pattern. These en echelon "C-rolls" are located directly across the Lehigh R. from the one sampled in this study.

interval. The conglomeratic sandstone is not as well defined here, but it is present and appears to thicken to the south as it does on the west side of the river. Also, a similar non-concordant red zone was present above the mineralized zone, but the steepness of the outcrop prevented accurate diagramming.

A half mile south of the occurrences clustered around Icebox Creek, at the mouth of Tank Hollow, the conglomeratic sandstone is exposed and possesses a very regular upper contact. In this case, the base of the conglomerate is not exposed, but a peripheral red margin was clearly present adjacent to the top, forming a gradational red zone of 1 to 2 feet. Of particular importance here is the fact that substantial new uranium concentrations (10 by 2 feet, maximum of 4,000 cps) were discovered adjacent to the red altered zone, above the conglomeratic sandstone. Also notable is one concentration located 100 feet south of Tank Hollow near the railroad which appears to be contained within a green, micaceous sandstone interbedded within the conglomeratic sandstone. This seemingly isolated occurrence contains large amounts of secondary copper minerals and carbonaceous trash, neither one of which was noted in any other concentration in the study area.

A summary of the characteristics of these deposits includes the following:

- 1) Size ranges from small pods, less than one foot square, to single and en echelon "C-rolls" with several hundred feet of continuity.

- 2) The uranium is located in gray-green sandstone, marginal to red alteration envelopes associated with irregularly shaped, channel-like beds of conglomeratic sandstone. Uranium occurs both above and below the altered conglomeratic sandstone.

3) A narrow zone containing the uranium concentrations parallels the margin of the red altered envelope which in turn is roughly parallel to the base of the conglomeratic sandstone bed.

4) The concentrations themselves have no visible identifying features and must be located by detecting their radiation. Only very rarely do they contain associated copper mineralization (as is common elsewhere in Pennsylvania) or obvious organic debris.

5) A narrow stratigraphic interval (less than 50 feet) contains all known concentrations to date, south of Penn Haven Junction. This interval is stratigraphically very near the Clark's Ferry-Duncannon contact.

Based on these conclusions, some speculation is offered on the location of yet undiscovered ore. Firstly, the contact between the Duncannon and Clark's Ferry would seem to be a primary target for exploration, because it already demonstrates an impressive areal relation to uranium. Secondly, the conglomeratic zones associated with that horizon are considered to be of great importance. Considerable accumulations of uranium may be located along the lateral and distal edges of the large proposed paleostream system passing essentially north-south through the Lehighon-Christmans-Pohopoco Mountain quadrangle area. The Penn Haven Junction deposits are felt to be situated on the western lateral edge, but the eastern edge has not been explored, and the distal limits have not been recognized. In addition, other paleostream dispersal systems have been postulated and tentatively identified (W. Sevon, personal communication) but have never been considered in relation to uranium.

Distribution of Elements around the Mineralization

The distribution of trace, minor, and major elements in rocks within

the immediate vicinity of the uranium mineralization was studied by analyzing a suite of 37 hand specimens, short (4-6 inch) 1-inch diameter diamond drill cores and chip samples. Determinations of 20 elements plus Fe^{2+} were carried out (Schmiermund, 1977). Analyses are listed in Table 2. Background samples from the Penn Haven Junction area and elsewhere in the Christmans quadrangle are included for comparison.

Seven background samples taken from the upper Catskill Formation in other parts of the region averaged 4.2 ppm total uranium, with the highest value being 6.8 ppm. Within the ore zone, a selected specimen contained 5210 ppm U(t) and thus represents a 1000-fold enrichment over the background. The combined oxidized and transition zones average 10.2 ppm uranium. A Student's t test (Dixon and Massey, 1951, p. 102) using logged data shows that the enrichment in the oxidized and transition zones relative to background is significant at the 99.9% level.

Scintillation measurements show uranium to be most concentrated in the center of the zone, and the edges of the zone to be very sharp (Figure 5). This distribution differs from Wyoming deposits, which typically show the greatest concentration near the trailing edge with the leading edge being rather diffuse (Warren, 1971).

The boundary of the ore zone is sub-parallel to the edge of the oxidized zone at distances of between 10 and 20 feet near the apex of the roll and less than 1 foot along the "tail." Although the number of samples from the reduced zone is limited, a decrease in the uranium content with increased distance in front of the ore is indicated. Such a decrease may indicate that the oxidized zone is enriched relative to the reduced zone.

Figure 5. Generalized pattern of element distribution across the roll front at Penn Haven Jct. (Plate 1).

Figure 6. Detailed plot of U, Pb and Se values across the roll front at Penn Haven Junction. Samples are arranged in order of distance from the nearest boundary of oxidized, transition, ore and reduced zones.

Table 2

Major, Minor and Trace Element Compositions of Rock Samples
(see Figure 6 for relative location of samples)

Sample Number Element	5307	5308	5309	5310	5311	5312	5313	5314
U (total) (ppm)	10.5	5.0	9.3	12.6	186.8	1690.0	76.7	29.1
As (ppm)	0	0	0	0	0	1.	1.	0.
Cr (ppm)	128.0	33.	77.	65.	79.	46.	46.	61.0
Cu (ppm)	6.	3.	3.8	8.0	6.5	6.0	6.5	47.5
Fe (t) as Fe_2O_3 (%)	3.96	3.54	4.15	4.05	2.35	3.10	2.51	2.46
MnO (ppm)	470	510.	500.	545.	365.	510.	840.	450.
Ni (ppm)	63.	30.	50.	44.	44.	35.	--	38.
Pb (ppm)	9.	12.	13.	13.	858.	308.	11.	12.
Zn (ppm)	46.	43.	54.	61.	35.	44.	40.	41.
TiO ₂ (%)	0.68	0.41	0.45	0.51	0.63	0.47	0.64	0.67
SiO ₂ (%)	89.7	87.7	84.5	84.2	86.5	86.0	85.7	84.2
Na ₂ O (%)	0.10	0.10	0.07	0.16	0.18	0.22	0.11	0.10
K ₂ O (%)	1.05	0.90	1.20	1.25	1.35	1.30	1.35	1.40
Al ₂ O ₃ (%)	7.25	6.80	7.70	8.25	7.60	7.25	7.60	8.70
MgO (%)	0.79	0.72	0.94	0.98	0.62	0.80	0.65	0.73
CaO (%)	0.16	0.10	0.14	0.14	0.12	0.14	0.10	0.12
S (ppm)	162.	27.	1.	1.	62.	22.	20.	0.
Co (ppm)	17.	17.	26.	25.	23.	22.	30.	23.
Fe ²⁺	0.665	0.747	0.733	0.960	0.600	0.666	0.469	0.713
Fe ²⁺ + Fe ³⁺								
Mo (ppm)	2.	2.	0	0	2.	3.	0.	0.
Se (ppm)	--	1.	4.	1.	238.	92.	<1.	--
V (ppm) } Values for these two only exist for last 15 samples								
C (%) }								

Blanks = not determined

Table 2 (Continued)

Sample Number Element	5315	5316	5317	5318	5319	5320	5321	5322
U (total) (ppm)	8.6	7.0	8.7	11.5	26.5	8.9	347.	7.
As (ppm)	0.	0	0	0.	0.	0.	1.	0.
Cr (ppm)	48.	44.	50.	81.	46.	33.	64.	36.
Cu (ppm)	6.0	5.5	8.0	68.5	6.0	3.8	5.5	3.5
Fe (t) as Fe ₂ O ₃ (%)	3.30	2.62	3.05	3.50	4.50	3.30	3.05	2.20
MnO (ppm)	490.	570.	870.	475.	830.	595.	440.	700.
Ni (ppm)	34.	29.	36.	52.	32.	31.	47.	26.
Pb (ppm)	8.	8.	253.	15.	14.	7.	59.	13.
Zn (ppm)	37.	33.	42.	50.	39.	28.	48.	33.
TiO ₂ (%)	0.54	0.43	0.44	0.95	0.95	0.52	0.71	0.33
SiO ₂ (%)	84.5	87.0	85.7	80.0	84.5	85.0	81.5	88.5
Na ₂ O (%)	0.17	0.07	0.13	0.22	0.19	0.19	0.14	0.18
K ₂ O (%)	1.16	1.15	1.05	2.25	1.25	1.45	1.85	0.85
Al ₂ O ₃ (%)	8.50	6.40	7.10	11.1	6.65	6.75	9.10	5.80
MgO (%)	0.68	0.62	0.75	0.90	0.84	0.54	0.89	0.50
CaO (%)	0.08	0.34	0.10	0.10	0.30	0.18	0.10	0.20
S (ppm)	147.	32.	38.	11.	38.	47.	11.	11.
Co (ppm)	17.	15.	20.	32.	18.	20.	26.	11.
Fe ²⁺								
Fe ²⁺ + Fe ³⁺	0.676	0.729	0.732	0.523	0.585	0.505	0.652	1.01
Mo (ppm)	2.	3.	3.	2.	0	1.	2.	0
Se (ppm)	--	<1.	42.	<1.	--	--	<1.	--
V (ppm)								
C (%)								

Table 2 (Continued)

Sample Number Element	5323	5324	5325	5326	5327	5328	5329	5330
U (total) (ppm)	17.6	10.2	16.0	11.9	24.1	9.7	33.5	295.
As (ppm)	0.	1.	0.	0.	0.	2.	4.	13.
Cr (ppm)	47.	63.	84.	55.	60.	54.	61.	29.
Cu (ppm)	3.8	4.5	3.8	7.5	5.0	6.5	17.0	13.0
Fe (t) as Fe ₂ O ₃	5.55	3.30	3.85	4.12	4.42	2.55	2.50	3.32
MnO (ppm)	500.	480.	740.	630.	500.	770.	780.	700.
Ni (ppm)	49.	37.	50.	40.	36.	42.	39.	33.
Pb (ppm)	1122.	8.	60.	21.	13.	15.	42.	418.
Zn (ppm)	69.	31.	56.	53.	37.	53.	42.	54.
TiO (%)	0.51	0.54	0.60	0.86	0.39	0.37	0.38	0.36
SiO ₂ (%)	77.0	85.0	81.5	85.0	81.5	84.0	83.5	84.5
Na ₂ O (%)	0.11	0.10	0.19	0.17	0.06	0.09	0.17	0.15
K ₂ O (%)	1.60	1.45	1.75	1.0	1.40	1.55	1.55	0.75
Al ₂ O ₃ (%)	9.00	6.70	9.00	6.80	7.00	7.40	7.30	5.75
MgO (%)	1.28	0.57	1.05	0.89	0.63	0.71	0.71	0.90
CaO (%)	1.06	0.18	0.26	0.14	0.22	0.08	0.10	0.22
S (ppm)	15.	96.	22.	27.	200.	249.	211.	171.
Co (ppm)	32.	16.	22.	20.	17.	23.	20.	18.
Fe ²⁺	0.781	0.532	0.785	0.811	0.432	1.060	0.702	0.793
Fe ²⁺ + Fe ³⁺								
Mo (ppm)	5.	1.	2.	0	0	0	0	1
Se (ppm)	270.	<1.	9.	--	--	1.	<1.	--
V (ppm)								
C (%)								

Table 2 (Continued)

Sample Number Element	5331	5332	5333	5334	5343	5344	5345	5346
U (total) (ppm)	3.1	20.5	2.8	6.1	12.8	3.1	2.9	1.1
As (ppm)	4.	0	0	0	4.	0	0	0
Cr (ppm)	67.	77.	59.	62.	83.	28.	59.	10.
Cu (ppm)	29.0	27.5	8.0	9.0	15.75	3.8	13.0	6.3
Fe (t) (ppm)	4.10	4.65	4.70	4.57	4.72	2.95	4.60	1.25
MnO (ppm)	710.	560.	300.	550.	510.	460.	380.	510.
Ni (ppm)	48.	55.	46.	41.	52.	27.	46.	16.
Pb (ppm)	10.	6.	4.	4.	594.	8.	7.	3.
Zn (ppm)	61.	71.	72.	72.	59.	27.	43.	17.
Ti (%)	0.71	0.77	0.72	1.12	1.62	0.54	1.03	0.09
SiO ₂ (%)	79.5	77.5	78.0	79.0	70.5	87.5	78.0	92.0
Na ₂ O (%)	0.17	0.08	0.06	0.06	0.13	0.05	0.09	0.02
K ₂ O (%)	1.75	1.98	1.78	1.36	3.30	1.05	2.33	0.59
Al ₂ O ₃ (%)	9.75	10.0	9.75	8.50	15.10	5.50	10.30	4.15
MgO (%)	1.19	1.22	1.33	1.23	1.18	0.49	0.76	0.23
CaO (%)	0.24	0.10	0.16	0.20	0.80	0.04	0.00	0.00
S (ppm)	231.	40.	15.	27.	65.	13.	2.	11.
Co (ppm)	31.	25.	28.	19.	50.	16.	33.	10.
Fe ²⁺	0.840	0.685	0.780	0.768	0.473	0.459	0.328	0.622
Fe ²⁺ + Fe ³⁺								
Mo (ppm)	0	0	0	1.	0	2.	0	0
Se (ppm)	--	--	<1.	<1.	--	<1.	--	--
V (ppm)								
C (%)								

Table 2 (Continued)

Sample Number Element	5347	5348	5349	U4	U5	U6	U7	U30
U (total) (ppm)	7.9	10.9	1.5	6.8	3.5	6.5	3.7	1.1
As (ppm)	0	2.	0	1.	2.	0	1.	0
Cr (ppm)	67.	53.	30.	60.	39.	45.	45.	35.
Cu (ppm)	8.3	9.0	6.8	9.5	21.0	16.5	8.0	10.5
Fe (t) (ppm)	4.90	4.25	1.60	4.09	2.75	3.05	2.60	1.65
MnO (ppm)	600.	510.	245.	350.	450.	340.	510.	1120.
Ni (ppm)	44.	42.	19.	39.	30.	35.	28.	22.
Pb (ppm)	60.	5.	4.	6.	5.	5.	7.	12.
Zn (ppm)	64.	34.	20.	45.	42.	41.	36.	30.
Ti (%)	1.40	0.805	0.28	0.84	0.47	0.75	0.60	0.38
SiO ₂ (%)	80.0	82.5	87.5	79.0	82.5	82.0	83.5	88.5
Na ₂ O (%)	0.06	0.09	0.05	0.07	0.06	0.06	0.06	0.04
K ₂ O (%)	1.36	1.97	1.01	2.03	1.67	1.63	0.91	--
Al ₂ O ₃ (%)	7.85	8.65	5.40	9.5	8.9	8.9	8.05	5.75
MgO (%)	1.18	0.63	0.31	0.73	0.67	0.65	0.47	0.40
CaO (%)	0.10	0.18	0.00	0.47	0.04	0.04	0.69	0.01
S (ppm)	15.	15.	18.	94.	54.	87.	168.	105.
Co (ppm)	27.	27.	10.	25.	20.	19.	19.	11.
Fe ²⁺	0.741	0.313	0.764	0.429	0.577	0.415	0.243	0.0
Fe ²⁺ + Fe ³⁺	0	0	1.	1.	1.	1.	0.	0.
Mo (ppm)	0	0	1.	1.	1.	1.	0.	0.
Se (ppm)	--	<1.	--	--	--	--	--	--
V (ppm)	--	--	--	105.	55.	65.	50.	40.
C (%)	--	--	--	0.04	0.00	0.00	0.07	0.07

Table 2 (Continued)

Sample Number Element	U43	U44	U1	U2	U3	U20	U21	U22
U (total) (ppm)	4.0	3.9	1100.	607.0	7.7	5210.	9.3	56.0
As (ppm)	1.	0.	5.	--	18.	20.	3.	30.
Cr (ppm)	50.	81.	78.	85.	66.	80.	60.	90.
Cu (ppm)	44.5	10.5	17.0	29.0	415.0	7.0	15.0	18.0
Fe (t) (ppm)	2.45	6.05	2.83	2.27	3.28	4.56	2.90	1.74
MnO (ppm)	240.	1010.	730.	741.	670.	930.	460.	840.
Ni (ppm)	46.	67.	36.	62.	0.	42.	28.	29.
Pb (ppm)	4.	5.	856.	569.	12.	2690.	10.	92.
Zn (ppm)	61.	74.	50.	45.	55.	80.	61.	25.
Ti (%)	0.63	1.14	--	--	--	--	--	--
SiO ₂ (%)	81.5	72.0	--	--	--	--	--	--
Na ₂ O (%)	0.12	0.21	--	--	--	--	--	--
K ₂ O (%)	1.40	2.81	--	--	--	--	--	--
Al ₂ O ₃ (%)	10.1	15.5	--	--	--	--	--	--
MgO (%)	0.77	1.07	--	--	--	--	--	--
CaO (%)	0.01	0.08	--	--	--	--	--	--
S (ppm)	--	--	--	--	--	--	--	--
Co (ppm)	25.	42.	--	--	--	--	--	--
Fe ²⁺	0.308	0.130	--	--	--	--	--	--
Fe ²⁺ + Fe ³⁺	0	0	--	--	--	--	--	--
Mo (ppm)	0	0	--	--	--	--	--	--
Se (ppm)	--	--	130.	--	<1.	840.	--	--
V (ppm)	45.	85.	370.	260.	135.	390.	65.	60.
C (%)	0.00	0.00	0.13	0.45	0.04	0.08	0.09	0.19

Table 2 (Continued)

Sample Number Element	U25	U27
U (total) (ppm)	6.9	10.6
As (ppm)	0.	0.
Cr (ppm)	50.	52.
Cu (ppm)	5.0	0.0
Fe (t) (ppm)	2.28	2.37
MnO (ppm)	300.	149.
Ni (ppm)	23.	0.
Pb (ppm)	32.	29.
Zn (ppm)	28.	30.
Ti (%)	--	--
SiO ₂ (%)	--	--
Na ₂ O (%)	--	--
K ₂ O (%)	--	--
Al ₂ O ₃ (%)	--	--
MgO (%)	--	--
CaO (%)	--	--
S (ppm)	--	--
Co (ppm)	--	--
Fe ²⁺	--	--
Fe ²⁺ + Fe ³⁺	--	--
Mo (ppm)	--	--
Se (ppm)	--	--
V (ppm)	60.	185.
C (%)	0.60	0.00

Similar observations have been made by other investigators (Harshman, 1974).

The significant enrichment of the oxidized and transition zone relative to background and possible enrichment relative to the reduced zone may be due to the adsorption of uranium on the amorphous Fe(III) oxyhydroxides formed during the alteration and mineralization.

Of the elements studied, Pb and Se have the most pronounced association with uranium. All three elements are concentrated in the ore zone by factors of 100-1000 over background. However, anomalies in both Pb and Se persist farther on the inner oxidizing side of the ore zone than does U (Figure 6). Klemic et al. (1963) reported clausthalite (PbSe) in the ore zone. The atomic ratio of Pb/Se in samples with anomalous Pb and Se ranges from 1.2 to 2.5 and is consistent with occurrence of all Se in clausthalite. Either the clausthalite contains considerable sulfur in solid solution, or an additional Pb mineral is required to explain the Pb. Although some Pb was undoubtedly derived by radioactive decay of U, calculations indicate that only a small amount originated in this fashion. The isotopic composition of the Pb (Klemic et al., 1963) and the offset of U and Pb anomalies also indicate that most Pb was introduced by the mineralizing solutions.

Arsenic is enriched in the ore zone, and Cu and Mo show statistically significant correlations with uranium. Iron decreases within the ore zone by about 1.2% Fe, and $\text{Fe}^{2+}/\Sigma\text{Fe}$ increases from 0.4 in the oxidized zone to 0.95 in the transition zone; then decreases to about 0.75 in the ore and reduced zones.

Summary of Distribution of Uranium in Rock

The anomalous and ore-grade uranium is clearly related to the

location of the oxidized channel-filling conglomeratic sandstone. The highest concentrations are near the oxidation-reduction boundary marginal to this zone, but weakly anomalous amounts occur within the oxidized zone. Minor U showings appear to occur along the lower margin of the channel over a distance of about a mile. A large but weak anomaly appears to be defined by this zone and undoubtedly forms a partial source for the anomaly in stream sediments and water of the area (Rose et al., 1976). The uranium is accompanied by roughly equivalent amounts of lead and selenium, and by traces of As, Cu, and Mo. These elements appear to constitute possible guides to both ore concentrations and to the channel sandstones through which ore depositing solutions moved. These chemical features, along with the oxidized character and permeable nature of the rocks, may aid in recognizing such channels in drill core or areas of poor outcrop.

DEVELOPMENT AND APPLICATION OF A METHOD FOR DETERMINING THE FORM OF URANIUM IN SOILS AND STREAM SEDIMENTS

The distribution of trace elements among the various chemically and physically defined fractions of stream sediments and soils (exchangeable ions, Mn and Fe oxides, organic matter, clay, etc.) has been investigated by numerous workers (Rose, 1975). The purpose of such studies is to elucidate the mechanisms and processes affecting the mobility of trace elements in the surface environment and to interpret chemical analyses. In the case of geochemical prospecting for ore deposits, a knowledge of the mode and extent of secondary transport can be of great use in designing a sampling and analytical program capable of detecting the desired type of anomaly and in interpreting anomalies of uncertain origin. For instance, if the mode of fixation within the sediment is known for the particular element of interest, an analytical procedure can be devised to determine only that part of the total elemental concentration felt to reflect the proximity of an ore deposit. Or, the anomalous amounts of an element may be assigned a hydro-morphic or clastic origin, and the anomaly followed up accordingly.

Many different procedures are available for partial extractions of elements from sediments and soils (Rose, 1975). In this study, the content of uranium in 5 chemical extracts and 3 size fractions was measured on eight stream sediments. The analytical procedure is described in Appendix 1. Table 3 briefly describes the eight procedures and the phases intended for extraction by each.

Samples employed for the partition study were selected from the unused portions of sediment samples taken as part of a geochemical drainage survey in northeastern and northcentral Pennsylvania (Rose et al., 1976).

Table 3

Extraction Steps and Phases Intended to be Affected

I. MgCl_2 leach	(I) Exchangeable and adsorbed ions, primarily on clays, organic matter and Fe-Mn oxides
II. Sodium hypochlorite leach	(II) Easily decomposed organic matter, sulfides
III. Hydroxylamine hydrochloride leach	(III) Manganese oxides
IV. Hydrogen peroxide leach	(IV) Organic matter not fully decomposed by the sodium hypochlorite
V. Sodium dithionite leach	(V) Iron oxides
VI. -100 mesh/+325 mesh size fraction	(VI) Sand size fraction
VII. -325 mesh/+2 μm size fraction	(VII) Silt size fraction
VIII. -2 μm size fraction	(VIII) Clay size fraction

The survey covered four 7-1/2' quadrangles in two areas, one including the anomalous areas around Jim Thorpe in Carbon County and the other including those in Sullivan and Lycoming Counties (McCauley, 1957). Four samples, both anomalous and background, were selected from each area (see Table 4 for locations).

General Procedure

Sample weights of 5.0 g were used (except 4940, 2.0 g) and all treatments of each sample were carried out in a single 50 ml centrifuge tube. The procedure was cumulative, i.e., each successive reaction was carried out on the residue from the previous treatment, as described in Appendix 1.

A 1 M MgCl_2 solution was used to displace other cations from clay minerals, organic material, and Fe-Mn oxides instead of the previously used Na acetate because of the greater effect expected by a divalent cation like Mg^{2+} . It is also expected that Mg^{2+} is sufficient to displace uranium from clay structures (G. W. Brindley, personal communication).

Sodium hypochlorite at pH 7 was selected as the solvent for organic matter because it is not expected to affect manganese oxides (unlike H_2O_2) which were the main target for the subsequent step. However, after extensive repeated treatment of several organic-rich samples it was apparent that sodium hypochlorite was not sufficiently oxidizing to break down the more resistant organics.

For the removal of manganese oxides, hydroxylamine hydrochloride was employed according to the procedure described by Chao and Sanzolone (1973). This procedure employs conditions reducing enough to dissolve the manganese oxides, but not so strongly reducing as to dissolve iron oxides.

Table 4

Location of Stream Sediment Sampling Sites
(see Rose et al., 1976)

Sample No.	Location
From Carbon Co. Area:	
4855	Keipers Run, Blakeslee Quad., along Pa. 903
4867	Creek 1.5 mi. S of Penn Haven Jct., Christmans Quad., mouth of creek, near junction with Lehigh River (site 4779)
4940	Icebox Ck., Christmans Quad., mouth of creek, near junction with Lehigh River (site 4776)
4888	Wild Ck., Pohopoco Mt. Quad., before entering Penn Forest Reservoir, considered a background sample (site 4849)
From Sullivan-Lycoming Co. Area:	
4862	Meyers Run, Sonestown Quad., S. of Bad Hill near junction of Beaver Run, Lycoming Co. (site 4787)
5402	Meyers Run, Sonestown Quad., S. of Bad Hill near junction of Beaver Run, Lycoming Co. (site 4787)
4914	Meyers Run, Sonestown Quad., upstream, near head of drainage, 1 mile W. of Beaver Lake, Lycoming Co.
5215	Beaver Run, Sonestown Quad., 1/2 mile So. of Beaver Lake, Lycoming Co. (site 4792)

Following the removal of manganese oxides the stronger oxidizing capacity of hydrogen peroxide was used to remove the residual organic material left by the sodium hypochlorite treatment. The resulting reaction was quite vigorous, indicating a significant amount of organics still remained. Several repetitions were required for some samples until nearly all black material was removed.

The final chemical treatment was a sodium dithionite procedure (modified after Jackson, 1956) to dissolve iron oxides under strongly reducing conditions in a sodium citrate-sodium bicarbonate solution buffered to pH = 7.5. Because of the strongly reducing conditions and the excess sulfur introduced with the sodium dithionite there is danger of precipitating native sulfur, metal sulfides, and uranium from the solution if the pH is not maintained above 7.5 throughout the reaction. Even if no precipitate is produced immediately, metal sulfides or uranium may precipitate before the analysis is carried out, making it necessary to oxidize and acidify the solution (in that order) after removal from the solid residue. After a single treatment as described above, only a slight trace of pink (hematitic) color remained in several samples.

Following all chemical treatments, the solid residue was then separated into three size fractions, sand (+325 mesh), silt (-325 mesh/+2 μm), and clay (-2 μm) by sieving and centrifuging (McNeal, 1975).

Analytical methods for all fractions are described in Appendix

1. A portion of the original solution from each treatment was

acidified with HNO_3 and shaken with TBP (tri-n-butyl phosphate) to extract uranium into a uniform matrix suitable for delayed neutron activation analysis (Ishimori and Nakamura, 1963; Steinnes, 1975). The solid fractions were analyzed for uranium by delayed neutron activation (Rose et al., 1976).

The Partitioning of Uranium Among Sediment Phases

A graphic representation of the distribution of uranium in the eight fractions is presented in Figure 7. Table 5 provides the pertinent numerical data. The major contributing sources to the total uranium in the sediments are those decomposed by H_2O_2 (resistant organics) and $\text{Na}_2\text{S}_2\text{O}_4$ (iron oxides), plus the sand and silt fractions. The other three extractable fractions and the clay fractions contribute less than 20% of the total in each case. Three of the samples taken from the Carbon Co. area were from the vicinity of known or suspected anomalies, and each showed the highest proportion of the uranium to be fixed in the resistant organic and iron oxide fractions. Sample 4888, however, was taken from an area regarded as background and showed a high contribution from the sand fraction and very little from the chemically extracted fractions.

Variability in the total uranium content of the stream sediments arises in several ways. Variations in the amount of detrital uranium-bearing phases in the sediment, concentrations of uranium in the water, and the adsorption characteristics of the sediment can all contribute to the final observed variability.

Solid Fraction Variability

Uranium may be transported to the site of sediment accumulation in the form of unweathered minor constituents of the source rock. Zircon,

Figure 7. Graphic representation of the distribution of uranium in the fractions. Total length of bar indicates total ppm U in sediment sample; length of individual segments indicate contribution of that phase to total U concentration.

Table 5
Uranium in Stream Sediment Fractions,
as ppm in total sediment sample

Sample No.	Whole Sediment [U (tot)]	MgCl ₂ Fract.	NaOCl Fract.	H.H. Fract.	H ₂ O ₂ Fract.	Na ₂ S ₂ O ₄ Fract.	Sand Fract.	Silt Fract.	Clay Fract.	Total of All Fract. (ΣU)
4855	3.40	0.07	0.22	0.28	1.14	0.73	0.83	0.94	0.37	4.59
4862	4.50	0.09	0.31	0.21	1.40	0.90	0.59	1.11	0.40	5.01
4867	3.20	0.14	0.25	0.13	1.64	0.33	0.12	0.74	0.33	3.69
4888	2.60	0.11	0.20	0.06	0.20	0.21	1.48	0.63	0.18	3.07
4914	5.85	0.05	0.31	0.38	2.49	0.85	0.41	1.41	0.40	6.50
4940	4.50	0.02	0.56	0.21	1.33	1.35*	0.28	0.56	0.18	4.50*
5215	3.05	0.09	0.14	0.12	0.21	0.65	0.91	1.00	0.24	3.15
5402	3.15	0.06	0.24	0.22	1.12	0.72	0.65	0.83	0.34	4.13

* Estimated on basis of 0% error between U (tot) and ΣU.

Table 5 (Continued)

Sample Number	% Error $\frac{\Sigma U - U \text{ (tot)}}{\Sigma U}$	U (tot) (ppm = $\mu\text{g/g}$)	U (ext), ppm Acetic Acid + H_2O_2 (Rose et al., 1976)	% LOI
4855	+25.8	3.40	0.8	16.84
4862	+10.7	4.47	1.9	8.58
4867	+13.5	3.19	1.5	44.3
4888	+15.5	2.59	0.2	5.6
4914	+10.0	5.85	3.3	12.12
4940	0	4.49	2.5	28.1
5215	+ 3.1	3.05	0.7	3.7
5402	+23.8	3.15	---	6.36

apatite, allanite, uraninite, and other minor primary uranium minerals have been observed in the rocks at Penn Haven Junction; of these, only zircon and apatite are sufficiently resistant to withstand much weathering and transport. Small amounts of U may occur in the lattices of major minerals (feldspar, micas, quartz, etc.) or as tiny grains of accessory minerals included by major minerals. Uranium occurring in such resistant detrital minerals would be preserved mainly in the sand fractions with possibly a small amount in the silt fraction. The bulk of the clay fraction in stream sediments is usually produced during weathering from such parent minerals as feldspars, micas, etc., or from preexisting clay minerals. In this case, most of the clay in stream sediments was probably derived by weathering of clays and micas in the matrix of the graywacke. Depending on the stability of the original clay relative to the weathering environment, the sediment clays may contain some nonexchangeable uranium incorporated during the period of uranium mineralization.

The contribution of a particular fraction to the total U in a stream sediment is partly related to the proportion of that fraction in the sample. For instance, in mixtures of sand containing 1 ppm U and silt containing 3 ppm U, the silt would contribute only 0.3 ppm of the total of 1.2 ppm U for a sample containing 90% sand, but would contribute 2.7 ppm of the 2.8 ppm U total if the sample were 90% silt. Changes in proportion could have a large effect on the total U in the sediment.

In Figure 8, the U concentration in the sand, silt, and clay fractions is plotted against the proportion of that fraction in the sample. Data for samples from Carbon County are segregated from data for samples from Lycoming-Sullivan County. Within each geographic area, the sand and

Figure 8. Uranium content of sand, silt, and clay fractions in stream sediments vs. percentage of fraction in sediment. Sand and silt fractions from each area contain a characteristic U content. Silt and clay fractions from Carbon Co. are from site 4888, a background area.

silt fractions are seen to have a characteristic content of U, but because of differing proportions of sand and silt, their contribution to the total sample varies. Both sand and silt from the Carbon County sediments contain 2-2.5 ppm U. By comparison, in Lycoming-Sullivan County, the sand fraction is greatly depleted in U and the silt fraction enriched. These differences may reflect differences in the character of the Catskill Formation in the two areas, a larger contribution from the Pocono Formation in samples from Carbon County, or differences in characteristics of weathering and erosion in the two areas. In any case, variable ratios of sand to silt would appear to have negligible effects on background values of stream sediments in Carbon County, but significant effects in Lycoming-Sullivan County.

In contrast, the clay fractions vary considerably in concentration of uranium, from 1-3 ppm, but the proportion of clay in the samples is relatively constant at 10-20%. The content in the clay may reflect the U content of the aqueous environment in which the clay is formed.

Extracted Fraction Variability

The remaining variability in the total uranium concentration is produced by chemically extracted fractions and is largely explainable in terms of the exchange characteristics of each fraction (which may be different from area to area) and the concentration of uranium in the associated water. In this case, the resistant organic and iron oxide fractions are the most important (see Figure 7).

The data on uranium in organic material, in combination with determinations of uranium in water at most of the sites, allow a test on these samples of the relationship derived by Szalay (1964) for adsorption of

uranium on humic material. Szalay found that $U(\text{adsorbed}) = 10^4 U(\text{dissolved})$. Table 6 lists data on the uranium extracted from the organic fraction, the amount of organic material (estimated from %C x 2 or from loss on ignition) and the calculated concentration of uranium in the organic material. The latter value ranges from 5 to 31 ppm. Also included in the table are uranium contents of stream water at the sites. Only values measured recently by the resin method (Korner and Rose, 1977) are listed, because most earlier samples were at or below the detection limit of the fluorimetric method or were collected during an unusually dry period of high uranium values (Rose et al., 1976).

A graph of uranium in the organic material vs. uranium in water (Figure 9) suggests that a relation exists, but two samples (4867, 4888) are markedly aberrant, and the coefficient relating the two variables is closer to 10^5 than 10^4 . At site 4867, which falls at higher U (water) than the others, the only measured U value is 0.21 ppb on 3/22/76. At nearby site 4940, the water contained 0.16 ppb on 3/22/76 but much lower values of 0.04, 0.08, and 0.07 ppb on other dates. Probably the long-term average at site 4867 is considerably lower than 0.21 ppb. Similar considerations may apply to site 4888, for which the only water analyzed for U was also collected on 3/22/76. In view of the large changes with time recognized previously, such discrepancies are not unexpected.

The difference in slope from Szalay's experiments probably results from the analysis of uranium occurring within the organic matter rather than only that adsorbed on its surface. In previous work (Rose et al., 1976), a coefficient of 2.7×10^4 was estimated by assuming that the uranium content of background stream waters was 0.1 ppb (Rose et al., 1976). If the background

Figure 9. Uranium in organic matter vs. uranium in stream water, showing possible correlation and divergence from adsorption equilibrium of Szalay (1964).

Table 6 Data on U content of organic material, and U content of stream water at sites of fractionated sediments

	U organic ¹	%C ²	% organic ³	ppm U in pure organic fraction	U-water ⁵
4855	1.36 ppm	8.23	16.5	8.2 ppm	
4862	1.71	3.24	6.5	26.	0.2,0.22,0.32 ppb
4867	1.89	18.70	37.4	5.0	0.21, see text
4888	0.40		5.6 ⁴	7.1	0.25, see text
4914	2.79	4.49	9.0	31.	0.3, est. from 4862
4940	1.86	16.30	32.6	5.7	0.04,0.07,0.08,0.16
5215	0.35	1.62	3.2	11.	0.15, 0.18, 0.20
5402	1.31	2.33	4.7	28.	0.2, 0.22, 0.32

¹ Concentration extracted with NaOCl and H₂O₂, relative to total sample

² Analyzed by gasometric method (Rose et al., 1976, p. 4)

³ %C x 2

⁴ Estimated from loss on ignition (Rose et al, 1976)

⁵ Includes values from Korner and Rose (1977) and Price et al. (1976)

in waters is 0.05 ppb or less, as now seems probable, then the previous coefficient agrees with the present estimate of 10^5 within the statistical and analytical errors. Further work is needed to confirm these estimates, but the need of correcting background values of stream sediments for their content of organic matter, as outlined previously, appears justified.

A significant amount of uranium was extracted from the Fe oxide fraction, ranging from 0.2–1.3 ppm U, averaging 0.7 ppm, relative to the total sample. Data on the amount of Fe extracted in this step is not available, but in previous investigations (Rose and Suhr, 1971; McNeal, 1975), about half the total iron was extracted in this step. Total iron ranges from 0.9% (sample 4888) to 3.4% (sample 4940). If Fe in iron oxides is 1%, then Fe oxides (Fe_2O_3) are about 1.5%, and the average Fe oxide contains $0.7 \text{ ppm} / 1.5\% = 50 \text{ ppm U}$. This value is significantly higher than the average U in organic material (15 ppm). The iron oxide is thus preferred over organic material as a host for uranium, but is less significant in the total sample because it rarely exceeds a few percent of the sample, whereas 5% organic matter is commonly present, and tens of percent are present in some samples.

In previous surveys, an H_2O_2 -acetic acid leach was used to obtain extractable U and accentuate the anomalies. Figure 10 plots U extractable by the H_2O_2 -acetic acid leach against the combined NaOCl and H_2O_2 fractions. A good correlation along a 45° slope indicates that this leach is extracting primarily U in organic materials. The points would diverge further from the 1:1 curve if U extracted by $\text{Na}_2\text{S}_2\text{O}_4$ were included, suggesting that the leach does not appreciably affect the Fe oxide component. In view of the strong partition of U into Fe oxides, a treatment that extracted Fe oxides as well as organic materials might improve the contrast of anomalies. We plan some tests aimed at developing a simplified procedure.

Figure 10. Uranium extracted by H₂O₂-acetic acid leach vs. uranium extracted from organic fractions (NaOCl and H₂O₂ leach), showing correlation and approximate equality.

A COMPARISON OF SOIL AND STREAM SEDIMENT FROM A SMALL ANOMALOUS DRAINAGE BASIN

Geochemical surveys of uranium in stream sediment and water will be much more useful if the data can be interpreted at least semi-quantitatively in terms of the amount of uranium in the drainage basin. If erosion is proceeding uniformly over an entire drainage basin, the stream sediment should be a representative sample of average soil in the basin, or average rock from which the soil is forming, unless significant fractionation into the aqueous phase is occurring. The hypothesis that stream sediment is a representative sample of the soil has been verified for several other elements (Hawkes, 1976; MacKenzie, 1977; Polikarpochkin, 1970, 1972), but because uranium is more soluble in the surface environment than most other elements, a test of its behavior seemed desirable.

The test has been made in the drainage basin of Meyers Run, a 1 mi² basin draining into Beaver Run in the Sonestown 7-1/2 minute quadrangle in north-central Pennsylvania (Figure 11). Details of this investigation are reported by Mahar (1977). A geochemical survey of stream sediment and water in the region around this basin is reported by Rose et al. (1976). The Meyers Run drainage basin contains two small copper-uranium prospects and is underlain by nearly flat-lying red fine-grained sandstones and mudstones of the lower Catskill Fm. Minor fine-to-medium-grained gray sandstone is also present and forms the host for the uranium occurrences. The area was glaciated in the late Pleistocene, but till is only sporadically present and is locally derived, so that soils are essentially residual. The lower part of the valley is partly filled with colluvium, which has impeded the drainage and caused a poorly drained area in the middle of the basin.

Figure 11. Location of soil survey and drainage samples, Beaver Lake area, Lycoming Co., Penna.

A total of 40 soil samples were collected on a square grid at depths of 3-9 inches (Figure 12). Prior to collecting these samples, chemical studies of six soil profiles showed that no consistent enrichment or depletion of major elements occurred in the soil profiles of the area. The lack of chemically distinguishable horizons probably reflects the immature soil development in the relatively short post-glacial period.

Results of Soil Survey

The soils were analyzed by atomic absorption (Medlin et al., 1969) and delayed neutron activation (Rose et al., 1976). The results are listed in Table 7, and the uranium values plotted in Figure 13. The uranium map outlines a definite anomalous zone, although not all the mineralized zones were detected. A difficulty in interpreting the uranium results lies in the fact that the contour outlines a marshy zone in its southern part. This portion of the basin is rich in decaying organic matter, and it appears that the uranium being removed from the known mineralized zones is being transported to the marshy area and being deposited, perhaps with the organic matter and/or clays. The north end of the anomalous zone is not in the marshy area and was not previously known to contain mineralization.

Stream Sediments and Waters

The stream sediment samples for the basin were collected at the outlet of the basin at intervals between November 1974 and March 1976. The samples consisted of active sediment from a 100 ft. length of stream. The sediment was dried at 110°C, disaggregated and sieved through a 100-mesh sieve. Analytical methods were the same as those used for soils. Results are listed in Table 8. Samples from several nearby sites have been analyzed for comparison.

Table 7
Analyses of Soil Samples

Site	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	Na ₂ O %
1	78.3	12.3	4.21	1.08	0.41	0.81
2	77.6	12.9	4.07	1.03	0.41	0.79
3	75.5	13.4	5.51	1.21	0.93	0.63
4	79.3	12.7	3.93	0.89	0.27	0.59
5	77.7	13.8	4.03	0.92	0.26	0.61
6	78.1	12.7	4.20	0.99	0.84	0.59
7	74.3	13.1	4.54	1.29	3.05	0.90
8	78.6	13.3	3.60	0.95	0.20	0.65
9	78.1	13.3	4.14	0.91	0.20	0.63
10	78.7	12.6	4.33	1.11	0.14	0.60
11	77.3	13.6	4.76	0.99	0.24	0.64
12	77.8	13.3	3.86	1.11	0.24	0.79
13	81.2	11.6	3.42	0.77	0.14	0.65
14	76.2	14.0	5.01	1.04	0.56	0.50
15	82.5	11.5	2.60	0.70	0.12	0.58
16	79.0	12.1	3.85	0.86	0.84	0.68
17	74.3	15.7	4.36	1.46	0.30	0.77
18	78.1	13.2	4.68	0.95	0.15	0.58
19	78.1	12.3	4.93	0.97	0.42	0.65
20	77.3	13.9	4.45	1.01	0.31	0.49
21	74.4	14.3	5.59	1.35	0.67	0.50
22	82.1	11.2	2.46	0.74	0.30	0.68
23	80.1	12.3	3.50	0.79	0.19	0.67
24	72.4	15.3	4.95	1.78	2.12	0.68
25	78.5	13.1	4.15	0.86	0.18	0.73
26	78.5	13.0	4.06	0.90	0.10	0.81
27	77.7	13.4	4.62	0.97	0.18	0.68
28	76.5	13.5	5.57	1.02	0.19	0.58
29	76.0	14.3	4.56	1.02	0.69	0.65
30	74.8	14.2	4.97	1.20	0.54	0.91
31	77.0	13.6	4.64	1.04	0.27	0.71
32	82.8	9.9	3.82	0.42	0.23	0.56
33	72.3	16.2	6.72	1.24	0.18	0.51
34	77.1	14.1	4.33	0.93	0.14	0.63
35	77.0	13.8	4.76	0.91	0.10	0.64
36	78.0	12.3	4.64	0.91	0.32	0.90
37	78.4	12.7	4.60	0.79	0.10	0.75
38	77.4	12.9	4.94	1.17	0.14	0.69
39	78.7	12.4	4.46	0.98	0.39	0.65
40	73.7	14.6	6.23	1.41	0.21	0.71

Table 7 (continued)

Site	K ₂ O %	MnO %	TiO ₂ %	Cu (ppm)	Zn (ppm)	U (ppm)
1	1.99	0.09	0.83	35	52	3.4
2	2.15	0.09	0.91	28	31	5.0
3	1.58	0.28	0.92	40	128	3.2
4	1.17	0.25	0.90	65	90	3.0
5	1.37	0.47	0.92	35	105	2.7
6	1.11	0.46	0.97	33	164	2.9
7	1.24	0.72	0.88	38	220	2.3
8	1.61	0.09	0.93	36	78	2.9
9	1.53	0.27	0.89	37	95	2.7
10	1.45	0.16	0.89	30	72	3.4
11	1.41	0.11	0.94	38	95	3.5
12	1.76	0.12	0.93	73	80	7.7
13	1.24	0.10	0.92	47	66	3.2
14	1.67	0.13	0.93	40	94	2.8
15	0.95	0.05	0.98	32	49	2.9
16	1.42	0.39	0.93	45	135	3.4
17	2.09	0.05	0.94	44	84	11.8
18	1.37	0.09	0.89	45	97	3.0
19	1.51	0.12	0.96	37	87	3.1
20	1.25	0.27	0.99	37	100	2.6
21	2.20	0.05	0.97	38	107	2.9
22	1.41	0.10	1.00	30	59	3.3
23	1.34	0.08	0.93	35	95	2.8
24	1.84	0.08	0.87	34	116	15.4
25	1.48	0.03	0.93	33	78	3.2
26	1.64	0.04	0.98	49	82	3.2
27	1.53	0.08	0.92	45	101	2.7
28	1.60	0.10	0.95	42	106	3.4
29	1.66	0.24	0.93	44	31	2.7
30	2.26	0.10	0.95	58	87	4.4
31	1.75	0.06	0.92	57	109	2.8
32	1.10	0.04	1.05	47	53	2.8
33	1.73	0.24	0.90	50	121	4.1
34	1.68	0.08	0.97	37	108	2.9
35	1.84	0.05	0.96	37	94	3.1
36	1.98	0.07	0.92	44	114	3.3
37	1.68	0.04	0.96	35	87	2.9
38	1.76	0.05	0.94	35	81	3.5
39	1.42	0.10	0.94	40	110	2.8
40	2.06	0.06	1.02	61	128	3.4

④ Location of Soil Profile •¹⁸ Location of Soil Survey Sites

Figure 12. Location of soil samples, Beaver Lake Area.

X Copper-Uranium Occurrence • Concentrations in ppm

Figure 13. Uranium in soil samples, Beaver Lake Area.

Table 8
Analyses of Stream Sediment

Sample Number	Date	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	Fe ₂ O ₃
<u>4787</u>	11/14/74	81.9%	9.59%	0.50%	1.42%	0.96%	4.14%
(4931)	8/26/75	82.9	8.32	0.78	1.24	0.76	3.99
(5214)	10/4/75	82.3	9.82	0.44	1.56	0.83	4.87
(5216)	11/2/75	80.7	9.45	0.46	1.47	0.65	4.86
(5217)	11/25/75	81.5	9.23	0.26	1.46	0.77	4.62
(5237)	2/3/76	81.1	9.40	0.46	1.31	0.95	4.50
(5402)	3/20/76	81.2	9.3	0.45	1.10	0.95	4.11
<u>4914</u>	7/23/75	80.4	10.1	0.46	1.53	0.77	4.53
<u>4915</u>	7/23/75	80.9	9.8	0.39	1.35	0.81	3.97
<u>4916</u>	7/23/75	84.0	8.4	0.21	1.02	0.90	3.62
<u>4917</u>	7/23/75	--	--	--	--	--	--
<u>4918</u>	7/23/75	78.5	11.2	0.53	1.86	0.72	4.96
<u>4919</u>	7/23/75	83.6	8.75	0.17	1.42	0.87	3.43
<u>4792</u>	11/29/74	85.4	7.83	0.15	1.12	0.69	3.95
(4930)	8/26/75	81.6	9.42	0.23	1.56	0.77	4.0
(5215)	10/4/74	86.7	6.56	0.11	1.01	0.70	2.66
(5235)	2/3/76	82.7	8.51	0.48	1.52	0.75	4.05
(5400)	3/20/76	82.2	9.03	0.51	1.45	0.79	3.95
<u>4932</u>	8/26/75	84.6	7.99	0.13	1.13	0.89	3.01
(5219)	11/25/75	86.7	6.91	0.18	0.80	0.79	2.91
(5403)	3/20/76	85.7	7.51	0.16	0.05	0.80	3.05
<u>4793</u>	11/29/75	87.1	6.65	0.30	0.72	0.74	2.76

Table 8 (continued)

Sample Number	MgO%	MnO%	TiO ₂ %	Cu (ppm)	Zn (ppm)	U (ppm) (total)	U (ppm) (extract)
<u>4787</u>	1.16	0.31	1.01	42	100	4.5	1.6
(4931)	0.97	0.13	0.95	45	109	4.1	1.7
(5214)	1.16	0.16	1.00	44	55	5.0	1.5
(5216)	1.13	0.15	0.97	44	102	4.4	1.2
(5217)	1.02	0.11	0.98	50	102	3.9	1.1
(5237)	1.10	0.24	0.96	47	109	4.0	---
(5402)	0.98	0.13	0.99	43	101	4.7	---
<u>4914</u>	0.89	0.27	1.00	65	127	---	3.3
<u>4915</u>	0.95	0.83	0.95	47	72	---	3.3
<u>4916</u>	0.82	0.09	0.96	25	85	---	1.7
<u>4917</u>	---	---	---	---	---	---	3.2
<u>4918</u>	1.02	0.24	0.96	43	91	4.1	2.3
<u>4919</u>	0.71	0.08	0.93	47	72	4.0	2.3
<u>4792</u>	0.75	0.15	0.91	37	64	---	1.5
(4930)	1.18	0.20	1.03	44	59	---	1.0
(5215)	0.69	0.61	0.99	37	116	3.3	0.7
(5235)	0.81	0.25	0.95	39	65	3.9	---
(5400)	0.95	0.16	0.01	40	67	4.4	---
<u>4932</u>	0.78	0.10	0.94	44	78	3.1	0.9
(5219)	0.60	0.07	1.02	37	92	3.5	0.5
(5403)	0.72	0.11	0.95	40	85	3.6	---
<u>4793</u>	0.58	0.06	1.09	45	109	3.8	0.8

Stream water samples were also collected at the above-mentioned site. Two 200 ml polyethylene bottles were collected, one filtered (0.45 micron) and acidified (2 ml 10% H_2SO_4), and one untreated. On some sampling dates, a 7 ml sample was also taken in a polyethylene vial, which was later used in the delayed neutron activation determination for uranium. Due to difficulties in determining the low uranium concentrations of the stream waters, an additional 1 liter water sample was taken at the sampling sites starting in March 1976. These samples were analyzed for U by delayed neutron activation of ion exchange resins equilibrated with the samples (Korner and Rose, 1977).

Conductivity measurements (HACH model 2510 conductivity meter) and temperature measurements were taken in the field, and pH measurements and alkalinity titrations were performed on some dates by methods described by Rose et al. (1976). Ca, K, Na, Mg, Si, Fe, and Zn were determined by atomic absorption, and Cl by titration (Brown et al., 1970). Analyses are in Table 9.

Comparison of Soil and Stream Sediment

Comparison of the mean concentrations in the stream sediments (site 4787) and the soils of Meyers Run (Table 10) shows that the stream sediment furnishes a representative sample of the soil in the drainage basin for most elements. The largest deviation is shown by Al_2O_3 , with SiO_2 and Na_2O and possibly K_2O showing smaller but statistically significant variations. None of the differences are large. In particular, the differences in uranium concentrations are small and insignificant.

The enrichment of aluminum and possibly potassium in the soil relative to the stream sediment apparently reflects a greater clay content

Table 9

Analyses of Filtered Stream Waters

Determination	Sample Numbers							Mean	Std. Dev.
	<u>4787</u>	<u>4931</u>	<u>5214</u>	<u>5216</u>	<u>5217</u>	<u>5237</u>	<u>5402</u>		
Na (ppm)	1.73	2.56	2.37	2.21	1.89	2.16	2.32	2.17	.285
K (ppm)	0.68	0.75	0.91	0.88	0.43	0.53	0.58	0.68	.179
Mg (ppm)	0.78	0.97	0.69	0.72	0.69	0.60	0.72	0.73	.115
Ca (ppm)	9.35	13.70	8.85	9.05	8.32	8.86	8.43	9.50	1.88
Si (ppm)	3.0	3.0	3.1	3.5	3.6	3.1	3.2	3.21	0.241
Fe (ppm)	0.20	0.10	0.20	0.25	0.15	0.15	0.20	0.178	.049
Zn (ppm)	0.01	0.01	0.06	0.07	0.07	0.01	0.02	0.035	0.029
Cl (ppm)	3.5	4.5	4.0	6.0	3.5	7.0	6.0	4.92	1.40
HCO ₃ (ppm)	---	20	7	7	7	45	---		
pH	---	---	---	---	---	6.2	6.2		
Conductivity (μ mho/cm)	---	66	60	55	57	54	70		
U (ppb) (fluorimetric)	0.3	0.3	---	---	0.3	0.3	---		
U (ppb) (resin)	---	---	---	---	---	---	0.32		
Temperature (°C)	---	22	11	11	3	0	5.5		
Date (month/year)	11/74	8/75	10/75	11/75	12/75	2/76	3/76		

Table 10
Comparison of soils, stream sediments, and rocks from
the Meyers Run drainage

Element	Rock* Mean	Stream Mean	Sediment Std.dev.	Soil Mean	Std.dev.	t(soil-sed.)
SiO ₂	76.4 %	81.7 %	0.76%	77.5 %	2.4 %	<u>-4.21</u>
Al ₂ O ₃	12.67	9.30	0.47	13.2	1.19	<u>7.88</u>
Fe ₂ O ₃ (ΣFe)	4.41	4.44	0.36	4.45	0.82	0.03
MgO	1.37	1.07	0.08	1.02	0.23	-0.52
CaO	0.83	0.48	0.15	0.43	0.55	-0.22
Na ₂ O	1.10	0.84	0.12	0.67	0.10	-3.73
K ₂ O	1.91	1.37	0.15	1.59	0.32	1.64
TiO ₂	1.09	0.98	0.02	0.94	0.04	<u>-2.40</u>
MnO	0.20	0.17	0.07	0.15	0.14	-0.34
Cu		45 ppm	2.7 ppm	42 ppm	10.4 ppm	-0.69
Zn		97	18.8	95	33.9	-0.14
U		4.37	0.40	3.8	2.52	-0.55

Critical value of t is 1.67 at the 95% confidence level.

* Mean of 21 rock samples from the Beaver Lake area, as recorded by Mahar (1977, Table 4). Samples WR-5 and TIV-1 deleted because of unusually high Ca values reflecting carbonate concentrations.

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in the soil. Silica is enriched in the stream sediments apparently in the form of quartz grains weathering out of the fine-grained sandstone and siltstones to create a quartz-rich sediment. The SiO_2 concentration is 4% greater in the stream sediment than in the soil. This increase did not dilute the other elemental concentrations proportionately, since the two sets of concentrations are approximately equal. Instead, the Al_2O_3 concentration has decreased approximately 4%. The simple dilution of the sample by increasing silica would only explain a small part of this decrease. The alumina has to be either retained in the soil, resulting in enrichment of the soil in Al, or it has to be removed in the stream water as colloidal or dissolved material.

Table 11 gives the results of alumina and silica determinations on material collected on a Nuclepore filter used to collect one liter of water from site 4787 (Figure 11). The Al/Si ratio is considerably higher in this suspended material than it is in the stream sediments. A loss of Al-rich, Si-poor suspended material would explain the observed differences between soil and sediment.

A comparison of outflowing sediment and water with average rock in the drainage basin is also of interest. Rock samples representative of the drainage basin were not collected, but several suites of rocks collected near the U occurrences of the area are available (Mahar, 1977). An average of sandstones, siltstones, and mudstones is given in Table 10. Although these samples were not collected to be representative of the rocks in Meyers Run drainage, they are approximately representative of the Catskill in the area. Very similar averages were obtained from 16 rock samples of the Catskill Fm. in the Little Pine Creek drainage about 35 miles to the west

Table 11

Analyses of Al_2O_3 , SiO_2 , and U in suspended material filtered from 1 liter of water, Site 4787, using 0.4 μm Nuclepore filter

Sample	Wt. of ash	SiO_2	Al_2O_3	U	$\text{Al}_2\text{O}_3/\text{SiO}_2$
5275	4.6 mg	2.64 mg (57%)	0.70 mg (15%)	<0.05 μg	
Blank filters	0.7	0.6 (86%)	0.002 (1%)	<0.05 μg	
Net suspended sediment	3.9	2.04 (52%)	0.70 (18%)	0.05 g	0.35
Mean stream sediment					0.17

SiO_2 and Al_2O_3 determined by J. C. Devine, analytical chemist, Mineral Constitution Labs, The Pennsylvania State University.

Sample collected 8/18/76.

(Hornberger et al., 1971).

Comparison of the rock and soil values indicates little difference in Si, Al, Fe, Mn, and Ti contents but large depletions of Mg, Ca, Na, and K from the soils. Depletion of these elements is expectable in weathering to form soils. From 30 to 50% of the content of these elements is lost in forming the soil.

Because uranium is also a mobile element, it is likely that some uranium has been leached in forming soil from rock. However, in view of the adsorption of uranium to organic material, the proportion lost is probably smaller than for Na, Ca, Mg, and K. Thus, although the U content of sediment is a good measure of the U content of soil in a drainage, the sediments cannot be relied on as a quantitative estimator of the underlying rocks. However, a U ore body exposed to weathering can be expected to leave at least some anomaly in soils of the area, and this will produce a corresponding anomaly in the stream sediments. Results from the following discussion indicate that the mobility of uranium is relatively small compared to the above major elements.

Transportation of Uranium

Uranium is carried out of the drainage basin in stream sediment, stream water, suspended solids in stream water, and ground water. Analysis of the suspended solids collected by the 0.4 μm filter shows that suspended solids transport a negligible amount of U. Only 4 ppm suspended solids were found, and these contain <5 ppm U, which calculates to <0.04 ppb U in the total water sample. By comparison, the dissolved U in stream water is 0.2-0.3 ppb. Calculations indicate that the flow of ground water leaving the basin is about 1% of the surface discharge (Mahar, 1977). Since ground

waters from wells at the Meyer residence near the outflow of the basin contain only slightly higher U contents than the surface waters (Korner and Rose, 1977), the flux of uranium in ground water is also negligible.

The amount of uranium discharged in solution may be estimated from the measured uranium content of 0.27 ppb (average of determinations at Penn State and by Price et al., 1976) and stream flow. The flow of Muncy Creek at Sonestown is given as 26.82 inches/year averaged over the drainage basin (U.S.G.S., 1975). A stream flow of 1.7×10^{12} grams of water/year can be calculated for the 1 square mile drainage basin of Meyers Run, and a total discharge of uranium in solution of 460 grams/year. This value is most likely to err on the high side, because the stream flow of Muncy Creek is higher than most other basins of this region, and for most of the year, our measured uranium values were less than the detection limit of the fluorimetric method, which is 0.2-0.4 ppb (Rose et al., 1976).

The discharge of uranium in solid particles may be estimated from the uranium concentration of the stream sediments and the flux of sediment. Table 10 gives 4.4 ppm as the average value of total uranium in the sediment. Rose et al. (1976) give data showing that 1.6 ppm uranium is readily extractable with H_2O_2 and acetic acid. The sediment flux may be estimated from the sediment yields of about 130 tons/mi.²/year found by Reed (1971) for Elk Run and Corey Creek drainages, about 40 miles north of Beaver Lake. These streams have drainage areas of 10-12 mi.² and drain mainly Catskill and Chemung Facies rocks, and are therefore very similar to Meyers Run. The total relief is greater in the Elk Run and Corey Creek drainages, but Meyers Run has local steep slopes.

Using a sediment yield of $130 \text{ tons/mi.}^2/\text{year}$, the total sediment discharge from Meyers Run drainage basin is calculated to be 1.3×10^8 grams/year. The flux of total uranium in sediment is then computed to be 550 grams/year, and the flux of extractable uranium is 210 grams/year. Appreciable errors in the uranium content of the sediment are unlikely; the sediment flux might be in error by as much as a factor of 2 in either direction.

Based on these estimates, the flux of uranium in the sediment and in the water appear about equal, especially if the extractable uranium that is related to ore is considered. The uranium content of both sediment and water are therefore susceptible to variations in the partition of uranium between sediment and water. The greater stability with time of uranium values in sediment (Rose et al., 1976), in combination with the moderate to high proportion of uranium carried in this form, makes sediment seem the more attractive medium for semi-quantitative evaluation of the uranium content in the drainage basin.

The form in which other elements are transported is summarized in Table 12, using the flux of water and sediment estimated above and the composition of the sediment and water. Si, Al, and Fe are transported primarily in sediment (85-93% as sediment), Ca and Na primarily in dissolved form, and Mg, K, and U in subequal amounts of the two forms. This comparison suggests that uranium is not as mobile as Na and Ca in this basin. The amount of organic material in the sediment is probably an important parameter limiting the mobility of uranium, because 20% of the total uranium flux is extractable from the sediment by acetic acid- H_2O_2 treatment (210 g of a total 1010 g flux of U). In an arid region with little organic matter, the

Table 12

Form of Transport of Major Elements and Uranium from
the Meyers Run Drainage

Element	<u>Concentration</u>		<u>Flux (g)</u>		<u>% of total flux</u>	
	Sediment	Water	Sediment	Water	Sediment	Water
Si	38.5 %	4.2* ppm	5.0×10^7	$.71 \times 10^7$	87	13
Al	5.3	0.37*	6.9×10^6	$.63 \times 10^6$	92	8
Fe	3.0	0.18	3.9×10^6	0.3×10^6	93	7
Mg	0.61	0.73	0.79×10^6	1.2×10^6	39	61
Ca	0.46	9.5	0.60×10^6	16.1×10^6	4	96
Na	0.61	2.1	0.79×10^6	3.5×10^6	18	82
K	1.07	0.68	1.4×10^6	1.1×10^6	55	45
U	4.2 ppm	0.27 ppb	550	460	55	45
U (extr.)	1.6 ppm	0.27 ppb	210	460	31	69

* Includes contribution from suspended solids.

proportion in the water might be much larger.

Another method of evaluating the mobility of uranium is to examine the concentration of U in the dissolved solids of the water. The total dissolved solids in the stream waters are estimated to be about 40 ppm, based on 0.7 times a mean conductivity of 60 $\mu\text{mho/cm}$ (Brown et al., 1970). Similar values are obtained by converting the elemental concentration of the water to oxides. The 0.27 ppb U in the water calculates to about 6.8 ppm in the total dissolved solids, compared to 4.2 ppm in the sediment, an enrichment of $\times 1.6$. In contrast, Na is enriched by a factor of 6 in the dissolved solids, and Ca by a factor of 65. Thus, uranium is not as mobile as some of the major elements, but is much more mobile than Si, Al, and Fe.

TESTS OF SOLVENT EXTRACTION OF URANIUM FROM WATER

As an alternative to the uranium concentration procedure using an ion exchange resin or TBP extraction (Appendix 1), we made some preliminary tests using a liquid "ion exchanger" (a secondary amine, Amberlite LA-1, Rohm and Haas) dissolved in xylene, petroleum distillate, or kerosene (Merritt, 1971, p. 183-195). Kerosene gave the best results. The general procedure is as follows:

- (1) Collect 1 liter filtered water sample in modified 1200 to 1500 ml polyethylene squeeze bottle.
- (2) Acidify with 10 ml of 10% H_2SO_4 and add 10 ml of 2.5% solution of LA-1 in kerosene.
- (3) Shake 2 minutes and then allow at least 4 minutes settling time.
- (4) Squeeze off the floating kerosene layer into a polyethylene storage vial. This can be done at the end of a day if the water collection bottles are capped.
- (5) Pipette 5 ml aliquot of kerosene layer into a second polyethylene vial and heat seal.
- (6) Irradiate kerosene samples and standards in nuclear reactor and determine uranium content by delayed neutron method. Irradiation and counting procedures are the same as for stream sediment samples.

Advantages of the method are that steps (1) to (4) can be done in the field, and subsequent sample treatment is simpler and faster than that for ion exchange resins. Sensitivity is about .06 micrograms per liter using 1 liter water samples (see below).

Disadvantages are that the uranium is only about 90% extracted into the organic liquid phase for our test conditions, and extraction is time dependent. Consequently, one must run standard solutions and maintain constant procedure and reaction times. A typical partition function or extraction ratio (E) for 2 minutes' shaking is 844 for tests using a kerosene solution of LA-1 (tests 168-2, 168-3) where,

$$E = \frac{\text{U conc. in organic phase}}{\text{U conc. in aqueous phase}}$$

Blanks were prepared by shaking the kerosene:LA-1 solution with distilled water in order to determine the neutron counts of the kerosene solution. The mean blank of 10 readings taken on four different days is equivalent to $0.175 \pm .020$ $\mu\text{g U}$. The sensitivity of the method, arbitrarily estimated as three times the standard deviation of the blank, is about $.06$ μg per liter of water or $.06$ ppb.

Further tests are planned, using various types of natural waters to investigate possible interferences.

SUMMARY AND CONCLUSIONS

Uranium occurrences in the Catskill Fm. at both Penn Haven Junction and Jim Thorpe, Pa., are localized near the base of the Duncannon Member of the Catskill. This member is distinctive in sedimentology from the underlying members. At Penn Haven Junction, an oxidized channel-filling conglomeratic sandstone body appears to have controlled the uranium concentrations. Uranium is localized in reduced sandstones below, above, and laterally adjacent to this conglomeratic sandstone, which is inferred to have been a permeable conduit for oxidizing ground waters in late- or post-Duncannon time. The uranium occurs in roll-type deposits similar to those of Wyoming. Some sandstones within the channel appear to be slightly anomalous in uranium compared to those outside the channel. Lead and selenium are concentrated with the uranium in these roll-type deposits. The margins of the channel appear to contain a series of small U occurrences that constitute a relatively large geochemical target for soil, sediment, and water surveys.

The selective extraction methods previously used to determine the mode of occurrence of Cu, Co, Ni, Zn, and other elements in stream sediments and soils have been successfully adapted to uranium. Organic matter, Fe-oxides, sand, and silt are the major hosts for uranium in the samples investigated. Within individual areas, the concentration of uranium in the sand and silt is relatively constant, but changes in proportions of sand and silt change their contribution to the total sediment, as well as the uranium content of the total sediment. Fe oxides have a greater affinity for uranium than organic matter but are much less abundant in the total sample, so are less important overall. The uranium concentration in the organic matter is approximately 10^5 x the uranium concentration in the water.

Comparison of soil and stream sediment from the Meyers Run drainage shows that stream sediments are a good representation of the soils in the basin for major elements, Cu, Zn, and U. Stream sediment can therefore be used to evaluate semiquantitatively the average concentration of uranium in soils of a drainage basin. This relationship had previously been demonstrated as a good approximation for copper and other metals by Polikarpochkin (1971) and Hawkes (1976) and can now be extended to uranium, at least in climates similar to Pennsylvania.

Hawkes (1976) shows that if rate of erosion are constant throughout the drainage basin, and interchange between sediment and water is negligible, the strength of an anomaly in stream sediments is related to the area of the drainage basin and the area and strength of the source by the following relation:

$$Me_a A_a = Me_m A_m + Me_b A_b$$

where Me_a is the metal content of the anomalous sediment sample, Me_b is the metal content of background sediment samples, Me_m is the metal content of soil or rock in the mineralized area, A_a is the total area of the anomalous drainage basin, A_m is the area of mineralization, and A_b is the area of background metal contents in the drainage (Figure 14). The data from this study indicate that this relationship is closely approximated for uranium.

Because $A_a = A_m + A_b$, the variable A_b may be replaced and the equation rearranged to give

$$A_a (Me_a - Me_b) = Me_m A_m - Me_b A_m = A_m (Me_m - Me_b)$$

as shown by Hawkes (1976).

The terms on the left side of the above equation involve only observable aspects of the stream sediment and the drainage basin. Polikarpochkin

Figure 14. Diagram illustrating parameters of formula for intensity of stream sediment (after Hawkes, 1976).

(1970, 1971) has proposed that the product $A_a (Me_a - Me_b)$ be termed the productivity (P) of the sediment anomaly. The terms on the right of the above equation express the area and grade (relative to background) of the mineralized source and are a measure of its total size and value, at least to the extent that it is exposed to weathering. The productivity of stream sediment anomalies can thus be used to evaluate the extent and grade of mineralized areas within a drainage basin. Although many combinations of A_m and Me_m can produce the same productivity value, a positive productivity significantly above statistical fluctuations is clearly of interest in exploration, and the greater the productivity, the greater the interest.

Polikarpochkin (1971) shows that the productivity of stream sediments remains approximately constant in a series of samples going upstream until the source is reached and then drops (Figure 15). The locations of multiple anomalies can be identified in this way. Attempts to apply this method in the Meyers Run drainage result in a very high P value for sample 4917, and constant but lower values for sites 4787, 4916, and 4919 (Figure 16). Sites 4915 and 4918 show much lower values. The very high value in 4917 may result from precipitation or adsorption of uranium on organic material in this vicinity, possibly from a nearby source or from collection of a non-representative sediment sample at this site. Re-collection of the sample, studies of the mode of occurrence of metals in the sample, and measurements of the uranium content of stream water above and below the site could be used to determine the origin of the anomalous productivity values in this and similar anomalies.

Comparison of rock and soil in the Meyers Run basin shows that significant fractionation of elements takes place in weathering the rocks, so that Ca, Na, Mg, and K are depleted in the soil. As a mobile element,

Figure 15. Productivity (P) of sediment samples along a stream in East Transbaikalia with multiple sources (after Polikarpochkin, 1971).

Figure 16. Productivity values for portions of Meyers Run drainage. X = Cu-U occurrence (northernmost site approximate).

uranium is expected to behave similarly, but the measurements of uranium flux in the sediment and water show that it is fractionated into the water less than Ca and Na. Calculations of the uranium content of dissolved solids in water lead to a similar conclusion. The strong adsorption of uranium on organic matter may be responsible for the relatively limited mobility of uranium.

In general, the agreement between soils and stream sediment, plus the other techniques described above, should allow semi-quantitative understanding and interpretation of uranium anomalies in stream sediment and an improved ability to follow-up sediment anomalies. The selective extraction technique should aid in understanding the source of anomalies.

Experiments with a liquid ion exchanger (Rohm and Haas Amberlite LA-1) indicate that this method can be used as a simple field method of concentrating uranium from natural waters. Trials of the method on natural water samples are underway.

APPENDIX 1

SEDIMENT PARTITION ANALYTICAL SCHEME

Figure 20 shows the overall procedure for the investigation of trace element partitioning into various fractions of stream sediments. Each step is discussed in detail below.

Samples -- Samples were selected from two areas on the basis of high uranium content as determined by neutron activation analysis of an acetic acid-hydrogen peroxide leach of the -100 mesh fraction of the sediment (Rose et al., 1976). For all but one of the eight sediments selected, 5.000 g of the air-dried -100 mesh fraction were used for the partition study (4940 contained only enough for 2.000 g). After weighing, the samples were placed in 40 ml, round bottom, pyrex centrifuge tubes, in which all extraction procedures were carried out.

Magnesium Chloride Extraction for Exchangeable Ions

Reagents: 1 M MgCl_2 solution, pH adjusted to 5.0 (203.3 g/l $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, pH adjusted with 0.3 N HCl).

Procedure:

- 1) Add 20 ml MgCl_2 solution to each sample, stir and suspend in ultrasonic cleaner bath for 30 minutes with occasional stirring.

Figure 17. Flow sheet for stream sediment partition analytical scheme

- 2) Place samples in centrifuge and spin at 2000 rpm for 15 minutes.
- 3) Decant supernatant liquid and any buoyant particles into 100 ml beaker. (Some black particles, presumed to be organic, floated in the MgCl_2 solution.)
- 4) Repeat steps 1-3 and combine supernatant in same 100 ml beaker.
- 5) Filter supernatant (Watman #41 filter paper) and return particles to centrifuge tubes.
- 6) Place combined supernatants in 50 ml volumetric flask (evaporated to less than 50 ml if necessary) and dilute to volume.
- 7) Retain in sample bottle as " MgCl_2 " fraction for analysis.

Note: Rubber stoppers were used to prevent evaporation and accidental spillage from the centrifuge tubes but were not allowed to come in contact with extracting reagent because of the high probability of contamination by Zn.

Sodium Hypochlorite Extraction for Organics

Reagent: 4-6% NaOCl, pH adjusted to 7.0 (Fisher Scientific,
4-6% NaOCl stock, pH adjusted with conc. HCl).

Procedure:

- 8) Add 20 ml NaOCl solution to residual material from previous extraction.

- 9) Stir carefully to avoid foaming and suspend in ultrasonic cleaner bath with intermittent applications of ultrasonics and stirring for 30 minutes.
- 10) Place in centrifuge and spin at 2000 rpm for 15 minutes.
- 11) Decant supernatant into 100 ml beakers.
- 12) Repeat steps 8-12 until no more visible change in organic content occurs (i.e. until no further lightening of sample color occurs). Required four repetitions on samples 4867 and 4940.
- 13) All supernatants were combined. After standing for several hours, several samples precipitated a fluffy, yellow-brown material from the combined supernatant (which resembled an amorphous iron oxide but proved negative with a Potassium thiocyanate spot test for iron). Because of the possibility that the precipitate contained trace elements from the solution it was reincorporated by the following procedure.
- 14) Evaporate the combined supernatant to dryness in a Teflon beaker, add 14 ml conc. HF and 10 ml HClO_4 (40%), heat with Teflon cover for 18 hours at just below boiling.
- 15) Uncover, evaporate to dryness and dissolve in 20 ml 1:1 (v/v) HNO_3 . Cover and warm for 12 hours at just below boiling. (Note: suggest using minimum volume

of HNO_3 in this step to avoid problems with a later neutralization step.)

- 16) Decant solution into 50 ml volumetric flask and dilute to volume with water.
- 17) Retain in sample bottle as "NaOCl" fraction for analysis.

Hydroxylamine Hydrochloride Extraction for Manganese Oxides

Reagents: Hydroxylamine hydrochloride, 0.1 M, pH adjusted to 4 (6.95 g/l $\text{NH}_2\text{OH}\cdot\text{CHl}$, pH adjusted with 2.5 N NaOH).

Procedure:

- 18) Add to residue from previous extraction 20 ml hydroxylamine hydrochloride solution, stir and suspend in ultrasonic cleaner bath for 30 minutes with occasional stirring.
- 19) Place in centrifuge and spin at 2000 rpm for 15 minutes.
- 20) Decant supernatant into 100 ml beaker.
- 21) Repeat steps 18-20 and combine supernatants.
- 22) Dilute supernatants to volume in 50 ml volumetric flask and retain in sample bottle as "hydroxylamine hydrochloride (H.H.)" fraction.

Hydrogen Peroxide Extraction for Organics

Reagents: Hydrogen peroxide, 30% H_2O_2

Procedure:

- 23) Added 10 ml 30% H_2O_2 to samples 4855, 4914, 5215 and 4862 which resulted in excessive foaming (contained in 1000 ml beaker). Then added 5 ml H_2O + 5 ml H_2O_2 to remaining samples which still resulted in excessive foaming which was similarly contained in a large beaker. (Note: recommend 5 ml H_2O be added to sample then H_2O_2 be added in 1 ml aliquots after reaction has subsided).
- 24) All material that foamed out of the centrifuge tube was washed into the large beaker and evaporated at 80°C to reduce the liquid volume for centrifuging.
- 25) After combining all material in the centrifuge tubes the samples were placed in the centrifuge and spun at 2000 rpm for 15 minutes.
- 26) Decant supernatant into 100 ml beaker.
- 27) Repeat 23-26 if visible organic material remains (4855, 4867 and 4940 were repeated).
- 28) Combine supernatant in 50 ml volumetric flask and dilute to volume. Retain in sample bottle as " H_2O_2 " fraction.

Sodium Dithionite Extraction for Iron Oxides
(Modified after Jackson (1956))

Reagents: Sodium citrate-sodium bicarbonate buffer
(39.6 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ + 6.89 g NaHCO_3 in 360 ml
 H_2O . Resultant pH = 8.3).
Sodium dithionite (sodium hydrosulfite) (Fisher
Scientific, powdered $\text{Na}_2\text{S}_2\text{O}_4$).
Hydrogen peroxide, 30% H_2O_2 .

Procedure:

- 29) Add to residue from previous extraction 20 ml of buffer solution and bring to 75–80° in a constant temperature water bath.
- 30) Add solid $\text{Na}_2\text{S}_2\text{O}_4$ in 0.5 g portions at 5 minute intervals with frequent stirring.
- 31) Place samples in centrifuge and spin at 2000 rpm for 15 minutes.
- 32) Decant supernatant into 100 ml beaker.
- 33) Adjust pH to 7.3–7.5 with NaHCO_3 (solid). (This step is necessary to avoid sulfur precipitation in following oxidation step. Samples 4888 and 4867 were not so adjusted and produced a yellow ppt. which was separated out.)
- 34) Add 5 ml 30% H_2O_2 to supernatant, cover and let stand.
- 35) Add 10 ml buffer to solid residue, stir and add 5 ml 30% H_2O_2 , agitate in ultrasonic cleaner and let stand 12 hours.

- 35) Place sample in centrifuge and spin at 2000 rpm for 15 minutes and combine supernatant with that from step 32.
- (Note: after standing at room temperature all samples produced a yellowish-brown, fluffy precipitate which necessitated the following digestion.)
- 36) Evaporate all samples to dryness at 95°C in oven, cool, add 5 ml conc. HNO_3 + 5 ml 30% HClO_4 + 5 ml H_2O and warm for 1 hour in covered beakers.
- 37) Evaporate to dryness and fumes of HClO_4 , then dissolve in 3 ml 1:1 (v/v) HNO_3 .
- 38) Dilute to 50 ml in volumetric flask and retain in sample bottle as " $\text{Na}_2\text{S}_2\text{O}_4$ " fraction.

Analytical Procedure

APCD-MIBK Chelation-Extraction System for Atomic Absorption Analysis (Modified after Koirtyohann and Wen, 1973)

Reagents: APCD 4% aqueous solution purified (2 g ammonium pyrrolidinecarbodithioate (Fisher Scientific) in 50 ml H_2O , shaken with MIBK to purify).

MIBK, 100% hydrated by shaking with water. (Methyl isobutyl ketone, 100% reagent grade stock).

Disodium hydrogen citrate-HCl buffer (pH = 2.5)

(solution A: 21.01 g citric acid in 200 ml
of 1 N NaOH, diluted to 1 liter.

solution B: 0.1 N HCl (8.62 ml conc. HCl
diluted to 1 liter).

buffer mixture: 35 ml solution A + 65 ml
solution B for pH = 2.5.

HClO_4 , 1 N

Standards: Multielement standards in MIBK (Prepared 5.0, 2.5, 1.5, 1.0, 0.5, and 0.2 ppm aqueous standards from 1000 ppm stock standards of Cu, Zn, Pb, Ni, Co, and Cr. Aqueous standards were then buffered, treated with HClO_4 , chelated with APCD and extracted into MIBK.

Procedure: All the following steps were repeated for each extraction fraction as quickly as possible to avoid the effects of unstable solutions noted by Koirttyohann and Wen (1973).

- (39) Place in 150 ml separatory funnels 50 ml of each standard + 50 ml of buffer + 100 μl , HClO_4 + 2 ml APCD and 50 ml MIBK and shake vigorously for 1 minute.
- 40) Allow phases to separate, draw off aqueous phase and retain MIBK phase in sample bottle.
- 41) In 60 ml separatory funnels place 20 ml of each sample, 20 ml of buffer, 100 μl HClO_4 + 2 ml

APCD and 20 ml MIBK and shake vigorously for 1 minute.

(Note: testing showed the buffer to be effective at maintaining the pH for all but the NaOCl and $\text{Na}_2\text{S}_2\text{O}_4$ fraction which contained HNO_3 . In those cases neutralization to a pH slightly above 2.5 was required before the buffer was added.)

- 42) Allow phases to separate, draw off aqueous phase and retain MIBK phase for analysis.

(Note: Depending on the amount of dissolved material in the aqueous sample capable of being chelated by APCD, a very dense MIBK phase may result requiring dilution with MIBK in order to promote efficient aspiration into Atomic Absorption unit. The $\text{Na}_2\text{S}_2\text{O}_4$ fraction was diluted with 20 ml MIBK and the H_2O_2 fraction should have been as some clogging of the aspirator tube resulted.

Analytical: The MIBK extracts were analyzed with a Perkin-Elmer Model 403 atomic absorption spectrometer, using a 2 inch burner head. Fuel flow was reduced to 20 divisions and air flow held at 55 divisions with MIBK aspirated between samples. The instrument was zeroed on the MIBK blank and standardized

with the MIBK standards described above. The height of the burner head was optimized for each element prior to the determination.

Testing showed all metal was extracted into the MIBK phase with none detectable in the aqueous phase of the standards. Also, a pronounced decrease in the A.A. response for Pb and Ni was noted if the standards were allowed to stand for several hours, requiring that all determinations be done as soon as possible after extraction. In all cases determinations were begun within 15 minutes after the final extraction had been completed.

Tri-N-Butyl Phosphate Extraction for Uranium with Neutron Activation Analysis

Reagents: Tri-n-butyl phosphate, 100% (TBP) (Fisher Scientific $(C_4H_9)_3PO_4$, purified).

- 43) In 60 ml separatory funnels place 10 ml of each sample + 4.83 ml conc. HNO_3 + 10 ml TBP, shake vigorously for 1 minute.
- 44) Allow phases to separate and collect all of the organic TBP phase, save for encapsulation in rabbits.
- 45) Using a pipette draw all of TBP phase out of sample bottle and transfer to two 5 ml polyethylene scintillation vials.

- 46) Heat seal scintillation vials and place both in rabbit and label.

Analytical: Delayed neutron activation analysis was carried out using the TRIGA MARK III REACTOR at The Pennsylvania State University coupled with an automatic sample transfer and counting system. Procedures, conditions and counting statistics are reviewed in detail in Rose et al. (1976).

Solid Fraction Separations

Procedure:

- 47) Transfer all residual matter from extraction steps onto a 325 mesh stainless steel sieve with minimal water. (Sieve placed on wide mouthed funnel over beaker.) Thoroughly wash fines through sieve with minimal water and collect in beaker.
- 48) Transfer residual matter from sieve into pan, dry and weigh. Save as Sand fraction.
- 49) Stir and homogenize filtrate slurry and pour equal volumes into even number of centrifuge tubes.
- 50) Centrifuge according to formulas provided by Jackson (1956) to settle out $+2 \mu$ particles and keep smaller particles in suspension.
- 51) Carefully decant off supernatant suspension using a large volumetric pipette and automatic pipette

bulb. Place suspension in a tared beaker and transfer residual matter from centrifuge tube in a tared beaker.

- 52) Evaporate contents of both beakers to dryness, cool in desiccator and weigh to obtain weight of silt (+2 μ) and clay (-2 μ).

Analytical:

- 53) Encapsulate up to 1.0 g of solid material from each fraction in scintillation vials for delayed neutron activation (see Rose et al., 1976) determinations for uranium content.
- 54) Weigh 0.5 g of each fraction into Teflon beakers.
- 55) Dissolve samples in 7 ml conc. HF and 5 ml 30% HClO_4 at temperatures just below boiling for 12 hours with Teflon covers.
- 56) Evaporate to dryness, take up in 10 ml 1:1 HNO_3 , heating to aid in dissolution. Dilute solution to 25 ml with water and save for trace metal analysis using atomic absorption spectrophotometry.

REFERENCES

- Allen, J. R. L., 1964, Studies in fluvial sedimentation: six cyclothems from the Lower Old Red Sandstone, Anglo-Welsh Basin: *Sedimentology*, v. 3, pp. 163-198.
- Ayrton, William G., 1963, Isopach and lithofacies map of the Upper Devonian of northeastern United States: in Symposium on Middle and Upper Devonian Stratigraphy of Pennsylvania and adjacent states, Shepps, Vincent C. (ed.), Pa. Geol. Survey, 4th ser., Bull. G39.
- Brown, E., Skougstad, M. W., and Fishman, M. J., 1970, Methods of collection and analysis of water samples for dissolved minerals and gases: in Techniques of water resource investigation, U.S. Geol. Survey Ch. A1, pp. 41-44.
- Burtner, Roger L., 1963, Sediment dispersal patterns within the Catskill facies of southeastern New York and northeastern Pennsylvania: in Symposium on Middle and Upper Devonian Stratigraphy of Pennsylvania and adjacent states, Shepps, Vincent C. (ed.), Pa. Geol. Survey, 4th ser., Bull. G39.
- Dixon, W. J. and Massey, F. J., 1951, Introduction to statistical analysis, McGraw-Hill, New York, 370 p.
- Epstein, J. B., Sevon, W. D., and Glaeser, J. D., 1974, Geology and mineral resources of the Lehigh and Palmerton quadrangles, Carbon and Northampton Counties, Pennsylvania: Pa. Geol. Survey, 4th ser., Atlas 195 cd, 460 p.
- Glaeser, J. D., 1974, Upper Devonian stratigraphy and sedimentary environments in northeastern Pennsylvania: Pa. Geol. Survey, General Geology Report G63, p. 89.
- Hawkes, 1976b, The downstream dilution of stream sediment anomalies: J. Geoch. Expl., v. 6, pp. 345-358.
- Hornberger, M. L., 1971, A geological, chemical and biological survey of the effects of land use on Little Pine Creek, Lycoming County, Pennsylvania: Report of student originated Studies Program sponsored by National Science Foundation and Penn State Univ., 310 pp.
- Klemic, Harry, Warman, J. C., and Taylor, A. R., 1963, Geology and uranium occurrences of the northern half of the Lehigh, Pennsylvania, quadrangle and adjoining areas: U.S. Geol. Survey Bull. 1138, 97 pp.
- Korner, L. A. and Rose, A. W., 1977, Radon in streams and ground waters as a guide to uranium deposits in Pennsylvania: Open file report GJO-1659-2, Energy Research and Development Adm., Grand Junction, Colo.

- Mahar, D. L., 1977, Geology and geochemistry of uranium occurrences near Beaver Lake, Sullivan County, Pennsylvania: M.S. thesis in Geochemistry, The Pennsylvania State University, 141 pp.
- MacKenzie, D. H., 1976, Empirical assessment of anomalies in tropical terrain: Assoc. Expl. Geoch. Newsletter, no. 21, pp. 6-10.
- McCauley, J. F., 1958, Uranium in Pennsylvania: Penna. Geol. Surv. Bull. M-43, 71 pp.
- Medlin, J. H., Suhr, N. H., and Bodkin, J. B., 1969, Atomic absorption analysis of silicates employing LiBO_2 fusion: Atomic Absorption Newsletter, 8, pp. 25-28.
- Merritt, R. C., 1971, The extractive metallurgy of uranium: Colo. Sch. of Mines Res. Inst., 576 pp.
- Polikarpochkin, V. V., 1970, Formation processes of secondary halos and dispersion flows in ore deposits: Ezheg., Inst. Geokhim., Siberian Otd., Akad. Nauk. SSSR 1970, pp. 300-313, in Russian.
- Polikarpochkin, V. V., 1971, The quantitative estimation of ore-bearing areas from sample data of the drainage systems: in Geochemical Exploration, ed. by R. W. Boyle, Can. Inst. Min. Met., Spec. Vol. 11, pp. 585-586.
- Price, V., Ferguson, R. B., and Baucom, E. I., 1976, Orientation study in the Williamsport, Pennsylvania, area: Open File report DPST-76-141-3 (GJBX-53), Energy Research and Development Adm., Grand Junction, Colo., 12 pp.
- Reed, L. A., 1971, Hydrology and sedimentation of Corey Creek and Elk Run basins, north-central Pennsylvania: U.S. Geol. Survey Water Supply Paper 1532E, 27 pp.
- Rose, A. W. and Keith, M. L., 1976, Reconnaissance geochemical techniques for detecting uranium deposits in sandstones of northeastern Pennsylvania: J. Geoch. Expl., v. 6, pp. 119-137.
- Rose, A. W., Keith, M. L., and Suhr, N. H., 1976, Geochemical drainage surveys for uranium: sampling and analytical methods based on trial surveys in Pennsylvania: Open file report GJBX-28(76) (GJO-1645-1), Energy Research and Development Adm., Grand Junction, Colo., 34 pp.
- Sevon, W. D., 1975, Geology and mineral resources of the Christmans and Pohopoco Mountain quadrangles, Carbon and Northampton Counties, Pennsylvania: Pa. Geol. Survey, 4th ser., Atlas 195ab.
- Schmiermund, R. L., 1977, Geology and geochemistry of uranium deposits near Penn Haven Jct., Carbon Co., Pennsylvania: M.S. thesis, The Pennsylvania State University, 153 pp.

- Szalay, A., 1964, Cation exchange properties of humic acids and their importance in geochemical enrichment of UO_2^{2+} and other cations: *Geoch. et Cosmoch. Acta*, v. 28, pp. 1605-1614.
- U.S. Geological Survey, 1975, Water resources data for Pennsylvania, Part 1. Surface water records (1974): U.S. Dept. of Interior.
- Warren, C. G., 1971, A method for discriminating between biogenic and chemical origins of the ore-stage pyrite in a roll-type uranium deposit: *Econ. Geol.*, v. 66, no. 6, pp. 919-928.

PLATE 1 - SECTION A-A'

HIGHWALL SECTION - S. OF PENN HAVEN J.

- Cr. grained and conglomeratic SS (no color distinction but generally fine to medium)
- Uniformly dark and light red or pink SS (no grain size distinction)
- Uniformly gray or olive to gray-green SS (no grain size distinction)
- Radioactive zones (800+ cps or 0.05-0.15 mR/hr)
- Aperts
- Grain Size Code
A fine - n. fine
B fine
C medium
D coarse - n. coarse (max. cong.)
E coarse - n. coarse (cong.)
- Bed, x-bed
- Color bed (Red)
- Limit of outcrop

ROCK SAMPLE LOCATIONS

- Diamond core or hand samples
- Channel-chip samples
- X High grade chip sample

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