

GLOO344

FC
USGS
OFR
80-
359

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.

Geochemical Exploration for Uranium
Utilizing Water and Stream Sediments

by

Karen J. Wenrich-Verbeek

Open-File Report 80-359

1980

Contents

	<u>Page</u>
Introduction.....	1
Sampling design.....	4
Sampling techniques.....	8
Stream sediments.....	8
Water.....	12
Analytical methods.....	22
Stream sediments.....	22
Water.....	24
Data interpretation.....	26
References cited.....	31

Illustrations

	<u>Page</u>
Figure 1. Map showing first, second, and third order streams for a low density detailed survey.....	7
2. Uranium is primarily concentrated in the less-than 90 μm size fraction.....	10
3. The distribution of uranium between mineral phases in various size fractions of stream sediments.....	11
4. Variation of the threshold shear stress with grain size.....	12
5. Sampling method for stream sediments.....	15
6. Uranium variation between filtered-unacidified and unfiltered-unacidified samples.....	16
7. Uranium variation between filtered-acidified and filtered-unacidified samples.....	17
8. Uranium variation between unfiltered-unacidified and unfiltered-acidified samples.....	18
9. Scatter diagram of Eh versus uranium, Ojo Caliente drainage basin, New Mexico.....	21
10. Frequency diagram showing normal and log normal distribution.....	27
11. The regional threshold for different populations of data.....	29

Tables

Page

Table 1. List of pathfinder elements commonly believed to be associated with uranium deposits.....	1
2. Samples collected at different times from the Rio Ojo Caliente near Ojo Caliente, New Mexico.....	20

Geochemical Exploration for Uranium Utilizing

Water and Stream Sediments

by Karen J. Wenrich-Verbeek

Introduction

Geochemical exploration for uranium applies the known geochemical properties of uranium to mineral exploration. The objective is to locate aureoles of uranium concentrations, or its pathfinder elements (table 1), sufficiently above normal to be identified as an anomaly. The anomalies may represent mineralization. Although the elements shown in table 1 are frequently associated with uranium deposits they only occasionally occur with uranium in hydrogeochemical or stream-sediment dispersion halos.

Table 1.--List of some pathfinder elements commonly believed to be associated with uranium deposits (modified from Levinson, 1974)

<u>PATHFINDER ELEMENT</u>	<u>TYPE OF DEPOSIT</u>
Se, V, Mo	U; sandstone type
Rn, Ra	U; all types of occurrences
Cu, Bi, As, Co, Mo, Ni	U; vein type

Two of the most commonly used sampling media in geochemical exploration for uranium are water and stream sediments. The application of water sampling to geochemical exploration is based on the high solubility of uranium in the oxidized 6+ valence state. The geochemical mobility of uranium is high; it is considerably more mobile than elements such as Cu and Zn. The concentration of uranium in oxidizing ground water tends to reach a value roughly proportional to the uranium concentration in the rocks through which it flowed. As ground water flows it tends to converge in streams and lakes so that, in general, a systematic sampling of surface waters allows detection of hydrogeochemical dispersion halos of buried uranium deposits. U⁶⁺ is not

coprecipitated during the precipitation of common minerals such as carbonates, sulfates and chlorides. Once uranium has dissolved in surface water the dispersion aureole is stable and persistent for many kilometers. Uranium has a high solubility over a large pH range due essentially to the formation of stable and soluble complexes of uranyl ions with the anions in natural waters (carbonate, phosphate, sulfate, and chloride). When in its reduced 4+ valence state uranium is extremely insoluble. Thus, uranium occurs in stream sediments not only as detrital minerals, but also it may be removed from solution through reduction to the 4+ valence state by organic material and incorporated into the stream sediment by adsorption onto the organic material. Under oxidizing conditions the following processes may produce a stream-sediment aureole of U at the expense of a hydrogeochemical aureole:

1. The precipitation of insoluble uranium minerals such as phosphates, arsenates, and vanadates,
2. The precipitation of uranium by insoluble hydroxides, such as those of Fe and Mn, and
3. The precipitation of uranium by organic matter.

Nevertheless, the removal of uranium from solution by adsorption and (or) precipitation is, in most cases, probably of minor importance compared to the amount of uranium contributed by detrital minerals. Stream sediments do not appear to have sufficient opportunity to adsorb significant amounts of uranium, even from high uranium waters, in moderate-to-high-gradient terrains (Wenrich-Verbeek, 1977a, b).

In general, stream-sediment anomalies indicate near-surface uranium deposits while surface water, because of ground water contributions through seeps and springs, also shows expression of buried uranium deposits.

The concentration of most trace and minor elements in natural water fluctuates widely in relation to changes in environmental conditions. For instance, in the more temperate Eastern United States the average uranium concentration in water is $<0.1 \mu\text{g}/\text{L}$ (ppb) whereas in the more arid Western United States the average uranium concentration is $>0.1 \mu\text{g}/\text{L}$. Although temperate climatic zones, such as the Eastern United States, favor the development of stable and easily detectable hydrogeochemical aureoles, dilution by rain water can be so acute as to "swamp-out" the anomaly or push the concentration of uranium below the lower detection limit. Semiarid climatic zones are in some respects ideal because (1) surface water flows for at least a significant part of the year and a sizeable percentage of this water is contributed by ground water rather than by rain water; (2) the uranium concentrations are sufficiently high so as to minimize contamination and analytical problems. Desert climates preclude the formation of a regular stream network--the water table is normally deep and ground-water movement is dominantly vertical--both of which prevent the formation of hydrogeochemical aureoles. In tropical climates the bedrock is generally deeply altered and leached making the detection of hydrogeochemical aureoles difficult. In cold climates the water circulation occurs mainly at the surface where accumulation of organic matter limits the formation of aureoles. This is due to the formation by the organic matter of a cap impermeable to oxidation, forcing the uranium to remain in the insoluble $4+$ state, as well as permitting the organic matter to adsorb what uranium may have been in solution. Climatic conditions for the various climatic zones vary greatly throughout the year, so the importance of prior evaluation of the geologic and climatic environment should not be underestimated.

Sampling Design

The sampling design, next to careful sampling, is perhaps the most critical part of an exploration program. If the sampling design is in error the entire program becomes irrecoverable. Whereas if the data interpretation is erroneous the results can still be reinterpreted.

Geochemical surveys can be divided into two main groups, reconnaissance and detailed, each requiring different considerations for sampling design. Reconnaissance surveys are applied to large areas from hundreds to tens of thousands of square miles and are relatively cheap and fast. Detailed surveys are used to focus on small parts of the reconnaissance area that resulted as favorable from the reconnaissance survey. Uranium deposits are much more difficult to isolate on a reconnaissance level, because of their generally small size and discontinuous nature, than are the larger more massive base- or ferrous-metal deposits. Hydrogeochemical and stream-sediment sampling are the most useful uranium reconnaissance-survey tools. Although water sampling is climatically restricted, stream-sediment sampling is available under most climatic conditions, and although samples from areas of at least moderate rainfall are preferred, sediments from dry stream beds are also useful and frequently are the only geochemical medium available to evaluate arid regions. Both of these media, as well as rocks and soil, can be used in a detailed survey although, in general, it is best to use dispersion media less mobile than water for detailed surveys. Water sampling is a powerful tool because of the high solubility of uranium when in the oxidized 6+ valence state. Water surveys can be of two types: (1) surface water and (2) ground water. Ground-water surveys should not be combined with those of surface water as the two water types have distinctly different chemical and physical properties; ground water tends to have higher contents of dissolved

components. Nevertheless, it is often useful to run both types as simultaneous studies. Ground water is a more reliable evaluator of the geologic terrane than is surface water, but it has many drawbacks. It is largely inaccessible in many regions, that is, there are no wells. When wells are available they rarely yield a good geographic or geologic distribution, but rather are usually restricted to localized areas tapping the same horizon. Well water also has the disadvantage of contamination, particularly from metals. Consequently, surface water yields a more random distribution of sampling sites and with careful sample design can yield excellent results. Lake water in the Beaverlodge uranium district, Saskatchewan, has been used for reliable delineation of zones of pitchblende mineralization within the Canadian Shield (Macdonald, 1969). Cold water seeps and springs as well as hot springs, although technically ground water, can be very useful in a surface water study because of their subsurface information and ease of accessibility as compared to wells. Sample design for surface waters is of the utmost importance. In areas of moderate to high rainfall (all perennial streams) sampling should be done during the time of year of lowest precipitation. In areas of abundant intermittent streams, sampling should be done when precipitation and snow runoff are low, but still sufficient for minimum discharge in the streams. This maximizes the contribution from ground water, which carries the information concerning buried uranium deposits. The entire area should be sampled as closely in time as possible in order to avoid fluctuations in stream discharge and permit comparison of all samples. Monthly stream discharge records are kept for most drainages in the United States by the United States Geological Survey and should be helpful in determining the time of year to sample.

The exact sampling density and particular regions to be concentrated on must be determined by the geologist familiar with both the geologic terrane and the topographic terrain on the basis of total budget and on previously available geologic, geophysical, and geochemical data. When designing the sampling program, site accessibility must always be kept in mind. Some sites can take as much as a day to reach, so their value, in exchange for 10 sites which might otherwise have been reached, must be carefully evaluated by the geologist.

Sampling should be restricted to first- or second-order streams, but preferably not both; streams of the same size should be sampled (fig. 1). Only under favorable circumstances should a sample represent a catchment area of more than 5 square miles (12 square kilometers). Streams that are 1 to 5 miles (1-8 km) long from their headwaters to the sampling point are ideal. In some regions of poorly developed drainage, catchment areas of 20 square miles (50 square kilometers) drained by 1- to 5-mile-long (1- to 8-km-long) streams, are not unusual. In this case 1 sample per 20 square miles (50 square kilometers) is acceptable. As a generalization, the larger the stream being sampled, the more extensive the mineralization must be to have a significant effect on the trace-element content of the water or stream sediments. For detailed surveys a sample density greater than one sample per kilometer of stream length is preferable. Every confluence is sampled, with sample sites located just above the stream junction far enough upstream to avoid contamination of the sediment from flooding of the adjoining drainage.

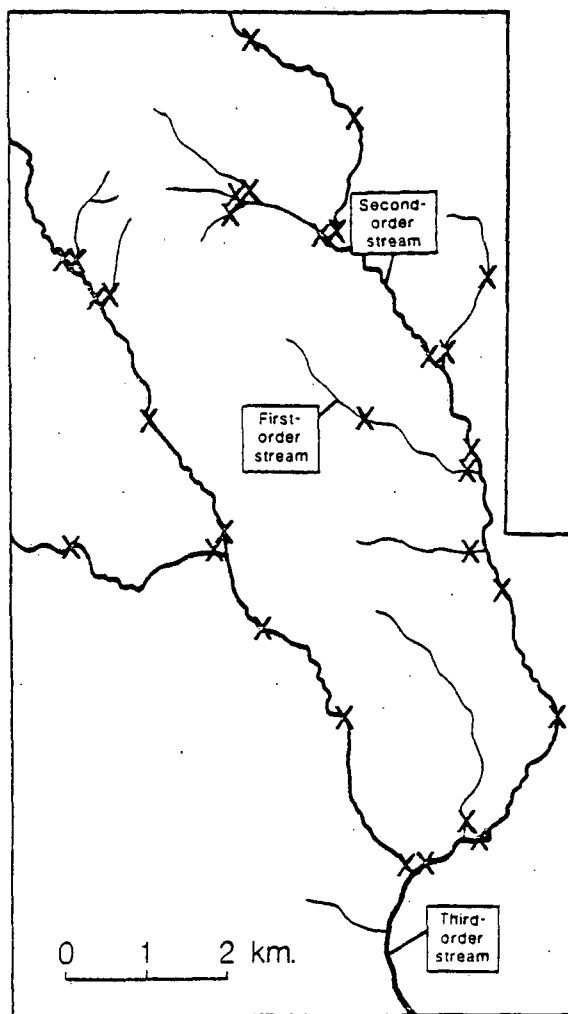


Figure 1. Map showing first-, second-, and third-order streams for a low density detailed survey.

Sampling Techniques

Stream Sediments: Stream-sediment sampling for uranium is more concerned with collecting the very fine fraction (fig. 2) than is sampling for the ferrous or base metals. This is due primarily

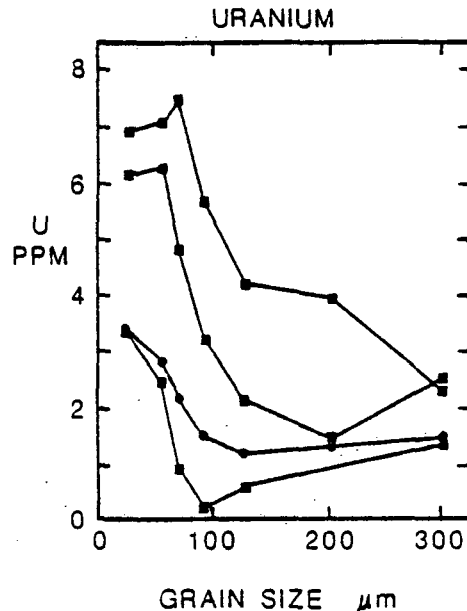


Figure 2.--Uranium is primarily concentrated in the less-than-90- μm size fraction (less-than-170 mesh) (Wenrich-Verbeek, 1977c, p. 349).

to three factors: (1) The extreme solubility, under oxidizing conditions, of such common uranium minerals as uraninite and pitchblende; (2) the high adsorption capacity of organic material and iron and manganese oxides for uranium in solution; and (3) the original fine-grain size and low resistance to physical weathering of most uranium minerals, particularly the common secondary minerals such as carnotite and tyuyamunite. Consequently, only the finest material, less than 88 μm (170 mesh), should be submitted for analysis. Rarely, uranium minerals do occur as large detrital grains in the very coarse fraction, greater than 200 μm . If the geologist believes this to

be true in an area, then this greater-than-200- μm fraction should be submitted for analysis. Nevertheless, figure 2 illustrates the tendency for uranium to concentrate in the extremely fine fraction; the break in slope toward high uranium concentration occurs at 90 μm . This tendency is exceptionally pronounced in streams rich in organic material. Figure 3 (D. L. Leach, written commun., 1977) shows that the leachable uranium is concentrated in the finest fractions, whereas uranium in zircon, as well as in other noneconomic minerals, is not. Using such a fine fraction necessitates a large sample, sometimes as much as 5 pounds. In high-energy streams sufficient fine material is sometimes difficult to locate, but if the stream is searched thoroughly, upstream from and under large rocks, sufficient material can be obtained.

Dry stream-sediment sampling is more complicated due to the problem of eolian contamination. Scraping off the top few millimeters only removes the contamination from the last windstorm, so another solution to the problem is necessary. Despite the contention from some geologists that the less-than-90- μm (170 mesh) size fraction, in contrast to the more standardly used less-than-177- μm (80 mesh) size fraction, contains more eolian contamination, the contrary is true. Figure 4 shows that a lower wind velocity is required to begin transport of the silt and clay size particles than the fine and very fine sand. This is because the clay- and silt-size particles are (1) held down more by cohesive forces than are sand-size particles and (2) they are smaller and therefore not affected as much by eddy currents of turbulent flow. Hence, the less-than-177- μm (80 mesh) size fraction contains a greater percentage of material located in the trough of the curve (fig. 4) than does the less-than-88- μm (170 mesh) size fraction. Nevertheless, both size fractions are readily transported by the wind and to avoid eolian contamination a coarse size such as greater-than-500 μm (35 mesh) and less-than-1000 μm (18 mesh),

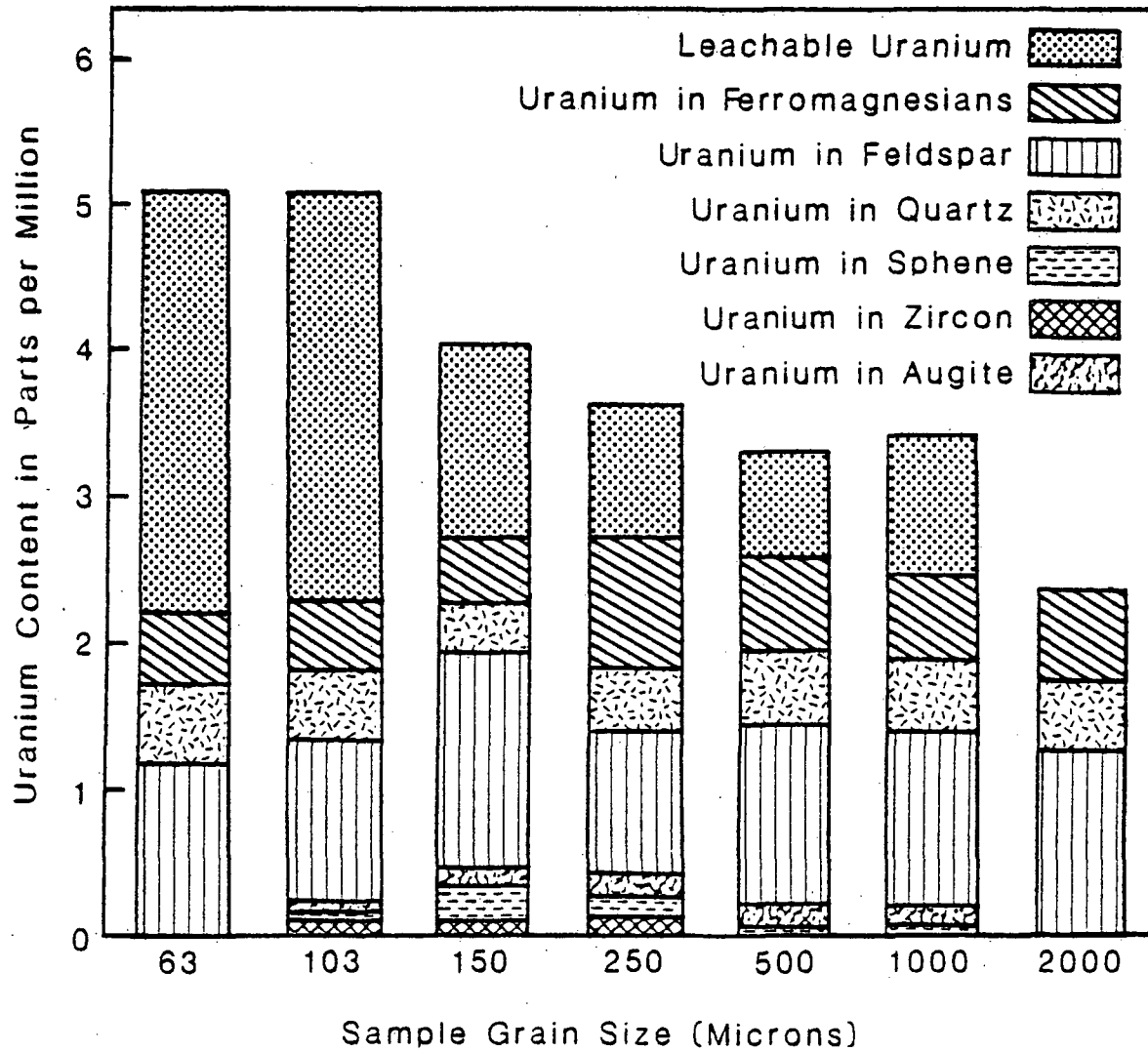


Figure 3. The distribution of uranium between mineral phases in various size fractions of stream sediments. (D. L. Leach, oral communication, 1977.)

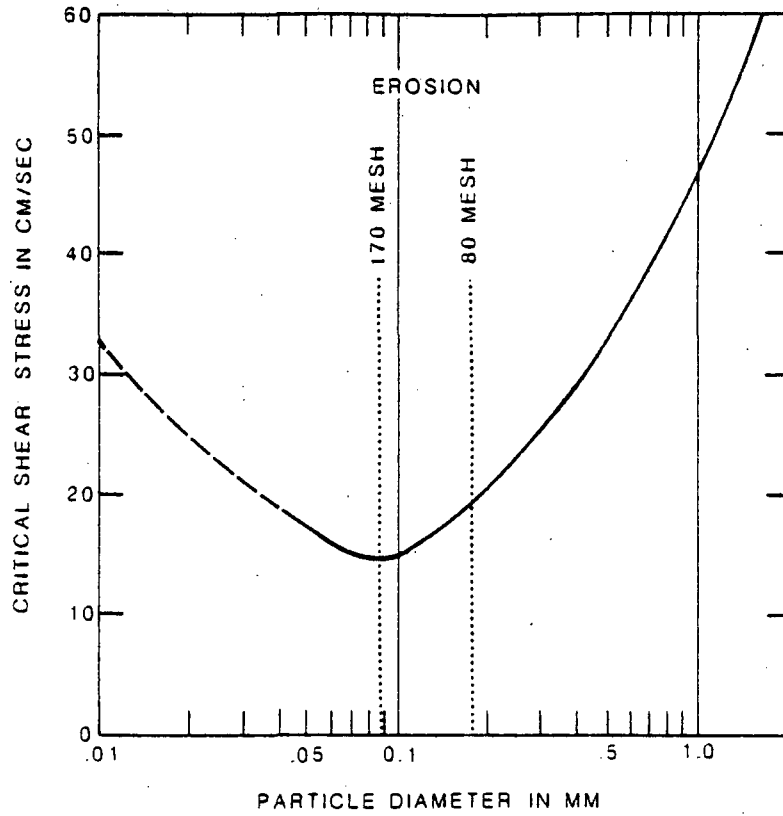


Figure 4. Variation of the threshold shear stress with grain size for air. (Modified from Bagnold, 1941, p.88).

coarse sand, has been recommended by D. L. Leach (oral commun., 1979) for sampling in arid environments. Figure 3 demonstrates that once the size fraction is coarser than 250 μ m there does not appear to be any significant change in uranium concentration until 1000 μ m is reached. Although this size fraction does not yield the greatest percentage of extractable uranium (fig. 3) it minimizes the more serious problem of eolian contamination in arid environments. Besides, due to the paucity of organic matter in arid regions, uranium does not appear to be as enriched in the fine fraction of the stream sediments as it is in more temperate areas (compare figs. 2 and 3).

Because of eddy currents, large physical and chemical inhomogeneities in the sediments within the channel, and migration of the active channel from the center of the stream, sampling cannot be restricted to one part of the stream. For the most representative sample, a composite sediment sample should be collected in a zigzag course across the channel beginning upstream and moving downstream along a length equivalent to on the order of ten times the width (fig. 5). Several grams of sediment should be taken along each segment of the path length to form the composite sample. Only the active sediments, those that are still being moved, should be sampled.

Water:

Problems of sample inhomogeneity are only minor with water sampling compared to stream-sediment sampling. Filtration is recommended to overcome the problem of changing concentration in solution due to leaching or adsorption of elements from the suspended fractions during storage, while acidification is recommended to minimize ionic species loss onto the container. Although these effects are minimal for clear water, they are not for turbid water, when filtration becomes essential for reproducible uranium determinations. If at all possible the collection of turbid water should be avoided.

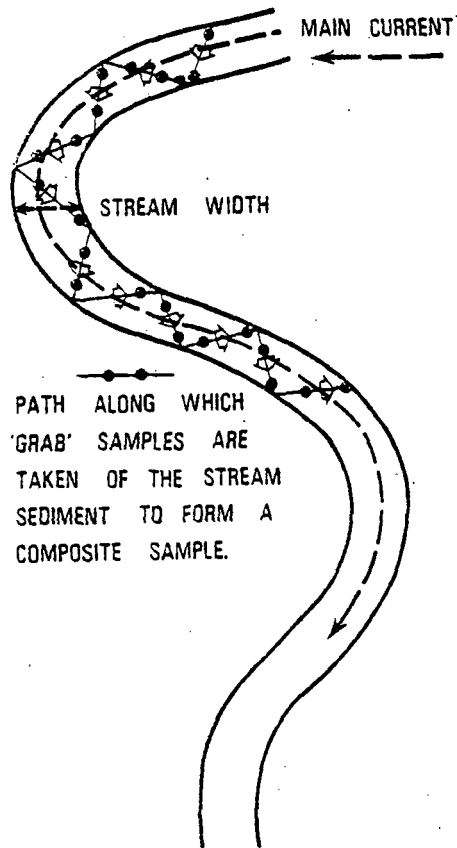


Figure 5. For the most representative sample the stream sediment sample should be taken as a composite sample along a zigzag course across the channel, beginning upstream and continuing along a length equivalent to on the order of ten times the width.

The variation in uranium concentration between a filtered and an unfiltered sample (both unacidified) can be seen in figure 6. In addition to turbid samples, those with low concentrations of uranium (less than $0.04 \mu\text{g}/\text{l}$) appear to have minor problems with inconsistent uranium concentration between unfiltered (later laboratory filtered) samples and field-filtered samples. This suggests at first glance that filtering might not be necessary, but a new problem is revealed by the data in figure 7. Figure 7 shows unacidified versus acidified samples for each site (all filtered). Many of the unacidified samples with uranium concentrations of less than $0.5 \mu\text{g}/\text{l}$ show a significant loss in uranium content as compared to the acidified samples. This is most likely due to adsorption by the polyethylene container of small amounts of uranium (probably on the order of less than $0.1 \mu\text{g}/\text{l}$) from the unacidified samples, whereas in the acidified samples the large hydrogen ion preferentially occupies the available exchange sites on the container walls. This adsorption effect is insignificant for higher concentrations of uranium, hence the insignificant difference between acidified and unacidified samples for uranium concentrations greater than $0.5 \mu\text{g}/\text{l}$. Thus, the samples should be acidified. Acidification of unfiltered samples should be avoided. With the exception of three turbid samples the acidified-unfiltered samples show a significant increase in uranium content (fig. 8)--a result of the lower pH allowing dissolution of a substantial amount of the uranium from the suspended material, which is later filtered out in the laboratory.

Samples unfiltered in the field and later filtered in the laboratory tend to either gain or lose uranium depending upon whether or not they were acidified. If unfiltered-acidified samples are used, most of the uranium, both dissolved and suspended, will end up in the filtrate, although this is

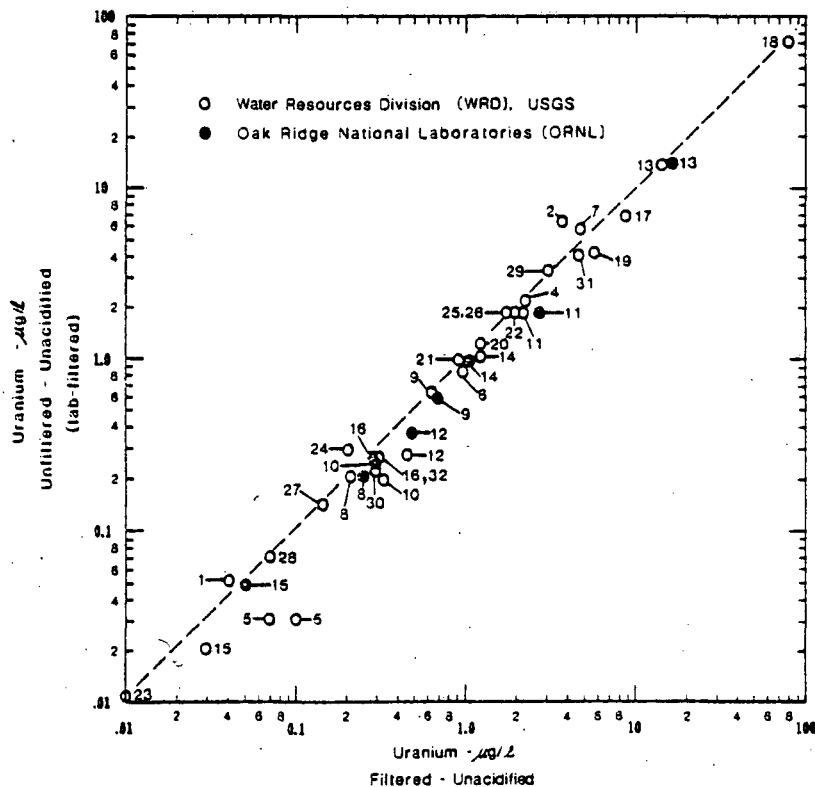


Figure 6. Uranium variation between filtered-unacidified and unfiltered-unacidified samples. The "unfiltered" samples were later filtered in the laboratory as compared to the "filtered" samples which were filtered in the field. Line represents the array of points where both sample types have equal uranium concentrations. A comparison of results on the same samples (number indicates sample site) by Oak Ridge National Laboratories (●) and the U.S. Geological Survey (○) provides an estimate of the precision of fluorimetric determinations.

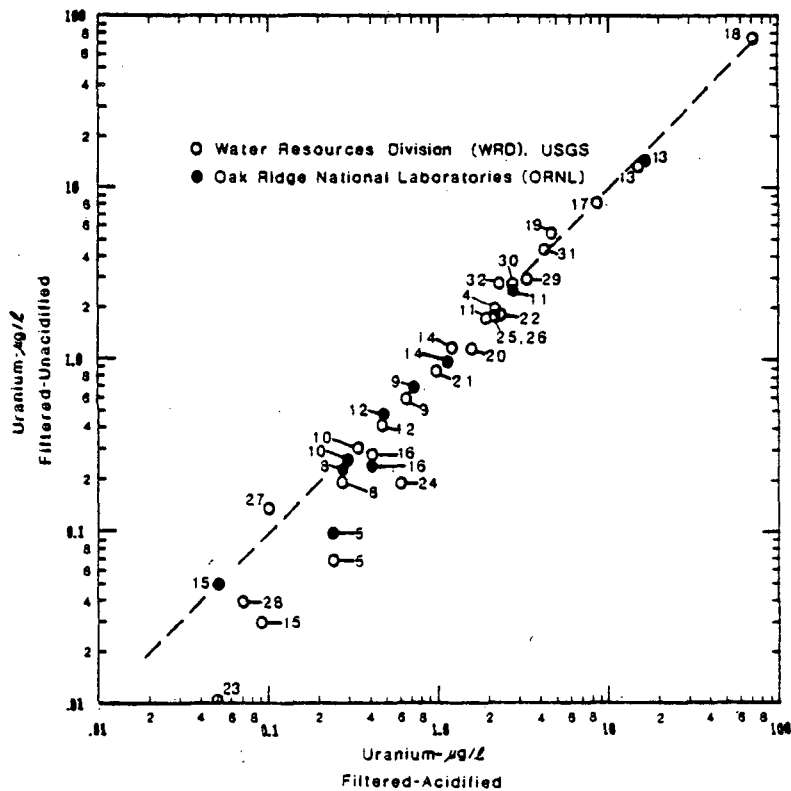


Figure 7. Uranium variation between filtered-acidified and filtered-unacidified samples. The "unfiltered" samples were later filtered in the laboratory as compared to the "filtered" samples which were filtered in the field. Line represents the array of points where both sample types have equal uranium concentrations. A comparison of results on the same samples (number indicates sample site) by Oak Ridge National Laboratories (●) and U.S. Geological Survey (○) provides an estimate of the precision of fluorimetric determinations.

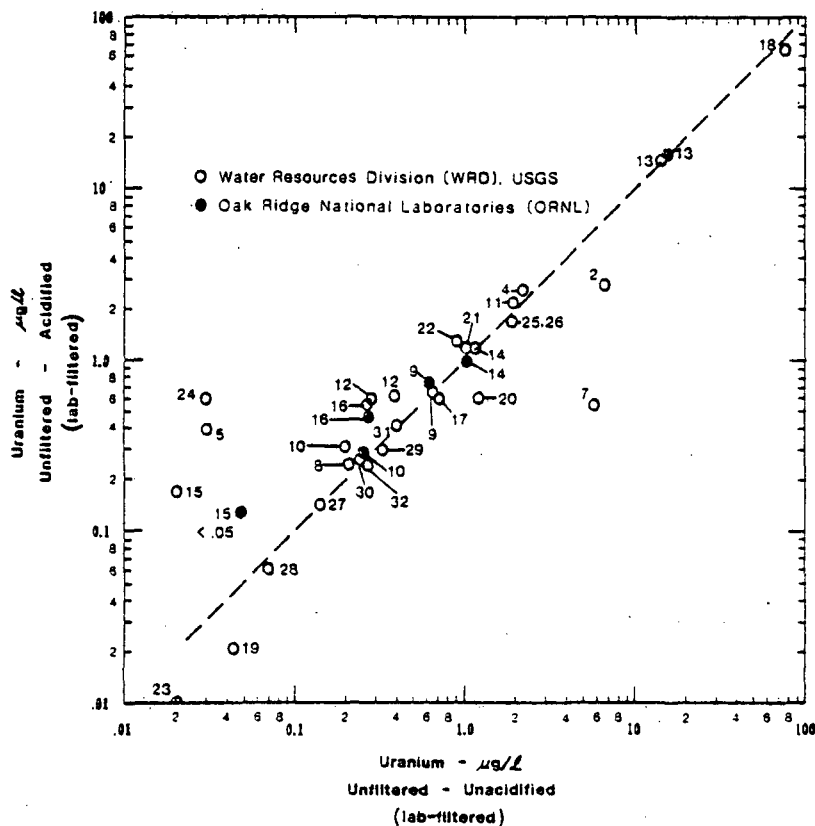


Figure 8. Uranium variation between unfiltered-unacidified and unfiltered-acidified samples. The "unfiltered" samples were later filtered in the laboratory as compared to the "filtered" samples which were filtered in the field. Line represents the array of points where both sample types have equal uranium concentrations. A comparison of results on the same samples (number indicates sample site) by Oak Ridge National Laboratories (●) and the U.S. Geological Survey (○) provides an estimate of the precision of fluorimetric determinations.

not always true and depends upon the nature of the suspended material. Due to these inconsistencies, for most uranium exploration a total leachate is not desired. Following such a procedure would result in the uranium content being totally dependent upon the quantity of suspended sediment in the stream. Sediment content is positively related to the surface runoff. A heavy rain upstream could thus result in more inconsistent changes in the uranium concentration of unfiltered-acidified samples than would filtered-acidified samples.

Although filtered-acidified, filtered-unacidified, and unfiltered-unacidified samples exhibit similar analytical results at concentrations higher than about $0.5 \mu\text{g}/\text{l}$, at lower uranium concentrations filtered-unacidified and unfiltered-unacidified samples tend to lose some of their uranium to the polyethylene container and to the suspended material. Thus, it is recommended that filtered-acidified samples be taken, especially for lower values of uranium. Because anomalous uranium in water associated with uranium deposits is occasionally as low as $0.5 \mu\text{g}/\text{l}$ and background must be determined in order to establish the anomaly threshold, values below $0.5 \mu\text{g}/\text{l}$ are important and need to be considered. If a stream is extremely clear, particularly in areas where helicopters are necessary and time is critical, it might be preferable not to filter (the sample should then not be acidified). In such circumstances, the entire study area must be treated the same, and the assumption is then made that a proportional quantity of suspended material is carried in each stream. This is not usually true and unless the suspended material is negligible there will likely result either some insignificant anomalous values or some that are overlooked.

Samples should be filtered through 0.45- μ m millipore filters into polyethylene containers. Passage of the water through the membrane must be accelerated by exterior pressure; if quantities of less than 50 ml of water are necessary (the volume of water is dependent upon the analytical method) then a plastic syringe, commercially available for water sampling, is adequate. Larger volumes may require a bicycle pump or a small nitrogen tank.

Acidification should be done using Ultrex nitric or hydrochloric acid. The sample should be acidified to a pH of approximately 1; low-ion pH paper is adequate to test the degree of acidification. A set volume of acid cannot be used because of the large variation in total dissolved solids from one sample to the next.

Conductivity measurements, which reflect the total dissolved-solids content of the water, are essential for a reliable uranium surface-water survey. Evaporation of surface water may greatly increase the uranium concentration, or a sudden rain may dilute it. This becomes a significant problem when a large geographic area is studied that requires more than a few days of sampling. In this situation variation in evaporation and discharge affect the resultant uranium concentrations. A practical method for minimizing those effects is to use conductivity measurements to normalize the uranium concentration. An example of fluctuating uranium concentration with changing discharge can be seen in table 2 for the Rio Ojo Caliente. These fluctuations were minimized by normalizing the uranium concentration by conductivity (last column, table 2). Hence, conductivity is the most important additional parameter needed; it can greatly increase the effectiveness of surface waters as an exploration tool by minimizing the external influences of evaporation and dilution.

Table 2.--Samples collected at different times from the Rio Ojo Caliente near Ojo Caliente, New Mexico

[1977 was a dry year, hence the low discharge during the month of May which typically has high discharge]

Date	Discharge	Uranium	Conductivity	$\frac{\text{Uranium}}{\text{conductivity}} \times 100$
July 23, 1975	15 ft ³ /sec	16 $\mu\text{g}/\text{l}$	715 $\mu\text{mhos}/\text{cm}$	2.2
May 19, 1976	109	3.3	235	1.4
May 5, 1977	9.2	30	1,100	2.7

Although field measurements of pH are useful for hydrology studies, their value in uranium exploration is questionable. No significant correlation between pH and uranium has been observed for streams studied throughout the United States (Ridgley and Wenrich-Verbeek, 1978). This lack of correlation is probably because the pH in surface water is rarely outside of the range of 6-8.5; this entire range falls within the same uranium species solubility field on the Eh-pH diagram of Hostetler and Garrels (1962). Thus, strictly for surface-water uranium exploration purposes pH has no applicability unless there is reason to suspect that the pH is outside the 6-8.5 range. If possible, pH values should be determined in case some values are outside of the 6-8.5 range; the measurements should be made in the field with a pH meter. pH paper, even low-ion paper, is not adequate because the total dissolved solids content in most natural water is so low that, generally, the results are not even close to the correct pH value.

Eh measurements in surface water have proved to be unreliable as well as useless to exploration. No correlation has been found between field Eh measurements and uranium concentration in surface water (fig. 9). Due to the constant oxidation of the platinum electrode by the oxidizing surface water, reproducible results are difficult to achieve. Consequently, the time-

consuming Eh measurements are not recommended for surface-water uranium exploration.

A composite water sample should be taken in one round-trip traverse across the stream. Ideally an integrated water sampler should be used, so that the water sample is representative of the total depth at the sampling locality. This is generally not necessary for first-order streams. For details on water and stream-sediment sampling see Wenrich-Verbeek (1976). Spring- and well-water samples should be taken as close to the point of issue as possible, before the water passes through any manmade softening or demineralizing devices. Water from pumped wells should be allowed to run for at least several minutes before sampling, until the temperature stabilizes, so that standing water in the system has a chance to be flushed out.

Analytical Methods

Stream Sediments:

Uranium concentrations in stream sediments can be determined by delayed neutron activation or by fluorimetry following an acid leach on the sediments. Delayed-neutron activation is not as frequently used because of the general inavailability of nuclear research reactors. It has the additional disadvantage of giving uranium concentrations as total uranium; this includes uranium tied up in such resistate minerals as zircon and samarskite, which are not amenable to present milling circuits in the United States. The advantage is the reproducibility and the knowledge that no uranium has been overlooked. If a multielement analysis is also made, delayed-neutron activation can be most useful in evaluating the mineral species, and hence the geologic terrane supplying the uranium.

Fluorimetry analysis on an acid leach of the stream sediments has an advantage for exploration in that it provides a total uranium content of only the "mineable uranium". The disadvantage is that exactly which minerals were dissolved and whether there was total dissolution of each phase is sometimes questionable. Also, some of the more resistate uranium minerals, such as brannerite, may not be leached and a possible deposit might be overlooked.

A good geochemical exploration program should have a multielement analysis. Furthermore, with the bulk of the exploration cost going toward field sampling it seems wasteful not to analyze the samples for other potential economic elements. In addition to these elements, determinations of organic carbon, Al, Fe, and Mn are desirable for removal of false anomalies. This is particularly true of organic carbon, which has such a strong affinity for the adsorption of uranium that samples taken from organic-rich pools within the stream often give anomalous uranium concentrations. These false anomalies can be removed if the organic carbon content has been determined. Determination of Fe and Mn serves the same function although their affinity for uranium is significantly less than that of organic carbon, so much so that they frequently do not have a significant correlation with uranium (Wenrich-Verbeek and Suits, 1979). Although uranium is also believed to be adsorbed onto clays, a significant positive correlation between Al and U is likewise not always observed (Wenrich-Verbeek and Suits, 1979). Elements correlating with uranium vary considerably among different geologic terranes. Those elements that generally correlate with total uranium in stream sediments are Th, Nb, Y, Ce, Yb, P, Li, Se, and Mg. Some other elements frequently correlating with uranium in more specific geologic terranes are Mo, As, Cu, Zr, Ag, Be, Cr, Ni, Pb, Sc, Ga, Zn, Ca and Ti. Elements such as Th, Nb, Y, Ce, Yb and Zr are present with uranium in the resistate minerals and are

therefore useful only for uranium determined by delayed-neutron activation. For instance, a large Zr enrichment with the uranium is indicative of a concentration of zircon in the sediments but not particularly indicative of uranium deposits. The elements As, Se, Mo, Cu and V are commonly thought of as associated with U in ore deposits. This association is principally in sedimentary uranium deposits, and hence, explains the lack of consistent correlation of these elements with uranium in stream sediments draining volcanic and metamorphic terranes. The Mg and Li correlation with U may be due to the presence of smectite clays (Glanzman, R. L., written commun., 1979); this is particularly prevalent in volcanic terranes.

Water:

Water samples may be analyzed for uranium by any of the following four methods: (1) extraction or direct fluorimetry, (2) neutron activation, (3) Scintrex* uranium analyzer, and (4) fission track. In the past, fluorimetry has been the most commonly used method. Direct fluorimetry determines uranium to a detection limit of 0.4 $\mu\text{g/l}$, the more expensive and time-consuming extraction fluorimetry has a lower detection limit of 0.01 $\mu\text{g/l}$. Unfortunately, extraction fluorimetry frequently requires one liter of water--a large sample. Neutron activation is generally more costly and requires the availability of a high flux nuclear research reactor. This method does have two distinct advantages: (1) a 0.01- $\mu\text{g/l}$ detection limit, and (2) no problem with loss of uranium into the container walls, as the entire container is irradiated. The Scintrex uranium analyzer has the advantage that it requires a small sample (although the sample must be

*Use of brand names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

filtered) and also it can analyze the sample immediately (in the field). Its disadvantage is a higher detection limit (advertised at $0.05 \mu\text{g}/\text{l}$) and the initial cost of the instrument. If 5000 samples are to be analyzed, the instrument becomes cost-effective. Although this is a field instrument, the laser beam can be knocked out of alignment if jarred excessively. Fission track has the disadvantage of requiring a nuclear research reactor and the track counting can be time-consuming unless an automated procedure is adapted. Nevertheless, this method is commercially available and has a detection limit of $0.01 \mu\text{g}/\text{l}$. Fission-track determinations of uranium give additional information on the location of the uranium in water. If the tracks are disseminated, the uranium is dissolved in solution whereas if they are in clumps the uranium is in the fine suspended material.

No matter which method is chosen, keep in mind that a detection limit on the order of $0.01 \mu\text{g}/\text{l}$ is essential unless there is good evidence that most water in the study area has more than $1 \mu\text{g}/\text{l}$ of uranium. Background values must be established and anomalies with values between 0.1 and $1 \mu\text{g}/\text{l}$ are not uncommon.

As with stream sediments, additional parameters are useful and necessary for the elimination of false anomalies in hydrogeochemical surveys. Because uranium is believed to complex with CO_3 , HCO_3 , PO_4 , SO_4 and F ions, analytical determinations of alkalinity (or HCO_3 or CO_3), PO_4 , SO_4 and F should be made. Phosphate is also important because uranium contained in phosphate fertilizers may be contaminating the water in agricultural areas.

Uranium in surface water most commonly correlates with the following cations: Ca, Mg, Na, K, Ba, B, Li, As. Although determinations of the major elements Ca, Mg, Na and K are of no particular use to exploration, determinations of Ba, B, Li and As are. Arsenic in particular, is the only

element commonly associated with uranium ore deposits that has a similar enough solubility to uranium to consistently correlate with it in surface water. This correlation may also be due to a complexing of uranium with arsenic in solution. The correlation of Li and Mg with uranium is probably due to the association of smectite clays and uraniferous tuffs or tuffaceous sediments in the aquifer system.

Data Interpretation

Geochemical exploration does not search directly for ore but rather for anomalies. If an anomaly is located it may indicate: (1) ore, (2) sub-economic accumulations of minerals, or (3) concentration of elements not representing mineralization, that is, a false anomaly due to secondary geochemical processes, sampling or analytical errors, or contamination. Although the use of a statistical analysis greatly helps in the interpretation of anomalies, a thorough knowledge of the geology and hydrology is the foundation for reliable interpretations.

The first step in data interpretation is the establishment of uranium background for a given area, sample type, or geologic terrane. Generally the modal value (fig. 10) is considered to be the normal abundance or background value. Before the mode can be determined it must be established whether or not the data is normally or lognormally distributed (fig. 10). Most geochemical data is lognormally distributed. Frequency histograms should not eliminate the "less than" data or valuable information is lost resulting in a higher mean value. The qualified, or "less than" data should be replaced for purposes of statistical analyses with an arbitrary value carefully selected that is less than the qualified value. The anomaly threshold value, the upper limit of background, also needs to be established. Values above the threshold

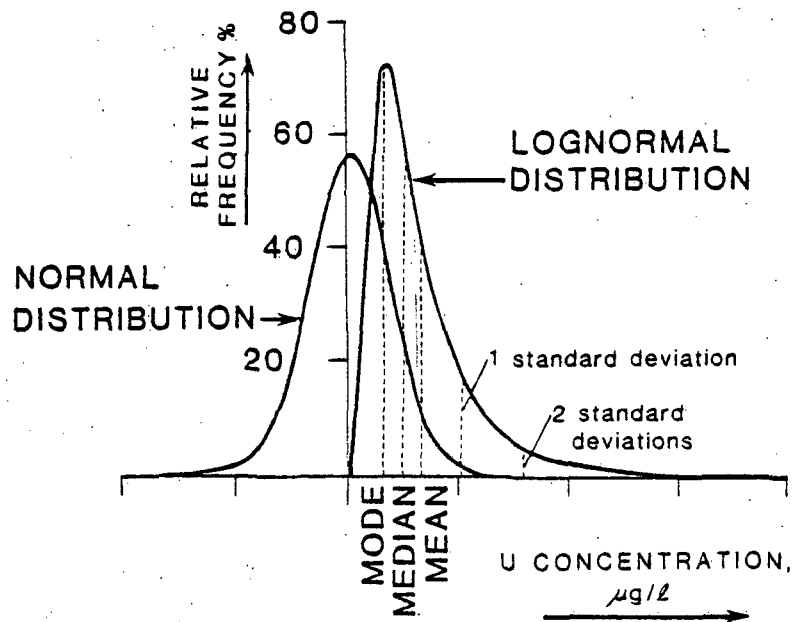


Figure 10. Frequency diagram showing both the normal and lognormal distributions.

are considered anomalous and worthy of careful scrutiny. The regional threshold and the local threshold are usually different, as can be seen from figure 11. Care must be taken not to mix populations, especially where one regional threshold is significantly higher than another and can obscure anomalous values if the populations are mixed (fig. 11). Cumulative-frequency plots can assist in isolating different populations. Determination of the anomaly threshold can be somewhat subjective. A number of rules have been proposed, although the two most commonly used are: (1) samples that contain amounts of elements twice background or more are anomalous (Boyle, 1971); and (2) samples that contain amounts of elements more than two standard deviations above the mean are anomalous (Hawkes and Webb, 1962). The latter definition is the most commonly used anomaly threshold in geochemical exploration, but the use of the mean value permits the anomaly threshold to be sensitive to extreme values; that is, one extreme value could force the anomaly threshold so high that no other data is anomalous.

The last step in data treatment is an attempt to eliminate false anomalies, sampling errors, and the like. Heterogeneity in stream sediments introduces false anomalies due to the varying proportions of such constituents as clay, organic matter, oxides, and carbonates, all of which have different fixation properties for uranium. In stream sediments the parameter most commonly causing false anomalies is organic carbon. A simple ratio of uranium to organic carbon can be used in place of the raw uranium data to eliminate false anomalies caused by high uranium content in some samples due to adsorption of uranium by large amounts of organic matter. A more ideal method is to use a weighted sum computed as a sum of all the above parameters plus uranium. If uranium was determined by delayed-neutron analysis the elements Th, Nb, Y, Ce, Yb and Zr may be added to the weighted sum in order to

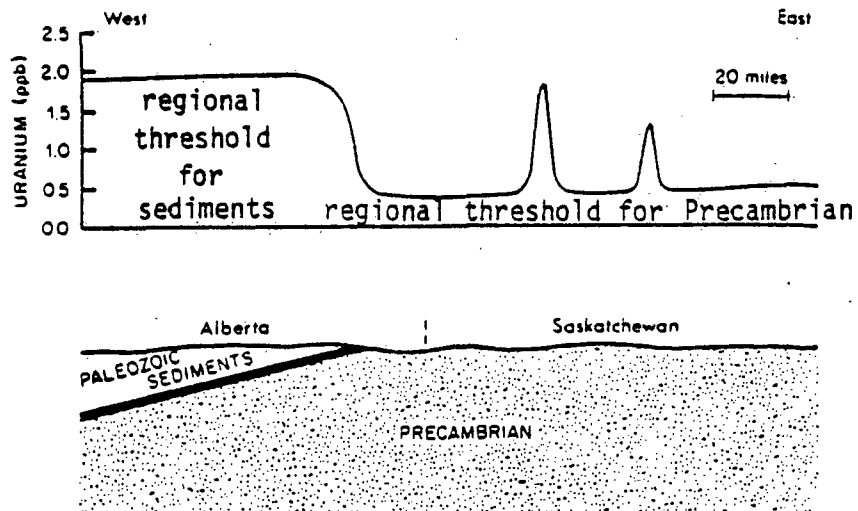


Figure 11. The regional threshold can be quite different for different populations of data. (Modified from Levinson, 1974.)

eliminate anomalies caused by large volumes of resistate minerals in the stream sediments.

Similar problems also result in false anomalies for hydrogeochemical data. As mentioned previously, fluctuating discharge may cause false anomalies. These may be eliminated by dividing uranium by conductivity (and multiplying by 100 or 1000 to make the number less cumbersome). If a stream suddenly enters a limestone terrane the uranium value will increase significantly; these anomalies may be eliminated by dividing by alkalinity, CO_3 , or HCO_3 . A stream entering an agricultural region may suddenly increase in uranium concentration due to uranium in fertilizers; dividing by PO_4 will minimize this problem. A multielement analysis combining these parameters as well as other complexing elements such as F and SO_4 is the best method for isolating true anomalies and eliminating variability due to environmental factors. Dall'Aglio (1972) showed an excellent example of multielement analysis of water samples. In his weighted sum he used Ca, Mg, Na, K (conductivity measurements may be substituted for these four elements), HCO_3 (alkalinity or CO_3 may be substituted), SO_4 and Cl. Fluorine, and particularly PO_4 , should be added to this list.

Because water and stream sediments evaluate different parts of the geologic terrane, both should be utilized simultaneously in a geochemical survey. Determining anomalous areas solely on the basis of the raw data is difficult and leads to false anomalies, as discussed above. Multielement statistical analysis is a powerful tool for data interpretation which should be applied to hydrogeochemical and stream-sediment surveys.

References Cited

- Bagnold, R. A., 1941, The physics of blown sand and desert dunes: Methuen and Co. Ltd., London, 265 p.
- Boyle, R. W., 1971, Geochemical prospecting, in, Encyclopedia of science and technology (3rd ed.): McGraw-Hill, v. 6, p. 124-129.
- Dall'Aglia, M., 1972, Planning and interpretation criteria in hydrogeochemical prospecting for uranium, in Bowie, S. H. U., Davis, Michael, and Ostle, Dennis (editors), Uranium prospecting handbook, p. 121-134.
- Hawkes, H. E., and Webb, J. S., 1962, Geochemistry in mineral exploration: Harper and Row, 415 p.
- Hostetler, P. B., and Garrels, R. M., 1962, The transportation and precipitation of uranium and vanadium at low temperatures, with special reference to sandstone-type uranium deposits: Econ. Geology, v. 57, p. 137-167.
- Levinson, A. A., 1974, Introduction to exploration geochemistry: Applied Publishing Ltd., 612 p.
- Macdonald, J. A., 1969, An orientation study of the uranium distribution in lake waters, Beaverlodge district, Saskatchewan: Colorado School of Mines Quarterly 64, p. 357-376.
- Ridgley, J. L. and Wenrich-Verbeek, K. J., 1978, Scatter diagrams and correlations of uranium in surface water versus discharge, conductivity, and pH at various locations throughout the United States: U.S. Geological Survey Open-file Report 78-581, 331 p.
- Wenrich-Verbeek, K. J., 1976, Water and stream-sediment sampling techniques for use in uranium exploration: U.S. Geological Survey Open-file Report 76-77, 30 p.

_____ 1977a, The effectiveness of stream-sediment sampling along the Rio Ojo Caliente, New Mexico, in Symposium on hydrogeochemical and stream-sediment reconnaissance for uranium in the United States: Grand Junction, U.S. Energy Research and Development Administration, DOE-GJO Document No. GJBX-77(77), p. 403-409.

_____ 1977b, Anomalous uranium in the waters of the Rio Ojo Caliente, New Mexico, in Short papers in the U.S. Geological Survey uranium and thorium research and resources conference, 1977: U.S. Geological Survey Circular 753, p. 73-75.

_____ 1977c, Uranium and coexisting element behavior in surface waters and associated sediments with varied sampling techniques used for uranium exploration: Journal of Geochemical Exploration, v. 8, p. 337-355.

Wenrich-Verbeek, K. J. and Suits, V. J., 1979, Chemical data and statistical analyses from a uranium hydrogeochemical survey of the Rio Ojo Caliente drainage basin, New Mexico; Part II, Stream sediments: U.S. Geological Survey Open-file Report 79-997, 125 p.