Uranium content and leachability of some igneous rocks and their geochemical significance

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Trace Elements Investigations Report 626

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Geology and Mineralogy

This document consists of 23 pages.
Series A

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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August 1956

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

USGS - TEI-626

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URANIUM CONTENT AND LEACHABILITY OF SOME IGNEOUS ROCKS AND THEIR GEOCHEMICAL SIGNIFICANCE

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ABSTRACT

The uranium content and its leachability in 442 igneous rocks of wide variety were measured. Four-gram samples, crushed below 38 mesh, were leached in 0.05 M HNO_3 for half an hour at 80 to 85° C; the leachate and undissolved residue were analyzed fluorimetrically.

This study explores the relation of uranium content and leachability to petrography. With few exceptions, the relations between uranium content, uranium leachability, rock leachability, rock type, and mineral composition seem to be random. Uranium content and leachability in homogeneous outcrops vary erratically; in heterogeneous outcrops the variation appears nonsystematic. Correlations with geologic environment indicate that uranium content and leachability are largely controlled by geologic processes during and after crystallization.

INTRODUCTION

This paper is a progress report on studies of the leachability of uranium from a large variety of igneous rocks under controlled laboratory conditions. The purpose of this study is (1) to investigate the possibilities of using leaching studies as a practical means of determining the quantitative fabric distribution of uranium; (2) to find the leaching technique(s) most likely to yield the desired information; (3) to document and accumulate knowledge on the fabric distribution of uranium in igneous rocks; (4) to test the usefulness of information on the fabric distribution of uranium to studies of the geochemical history of uranium in igneous rocks;

and (5) to determine if such information would be useful and in what ways it would be useful to the search for ore deposits.

To date, 442 igneous rocks, largely from the western United States and ranging in composition from ultramafic to felsic and feldspathoidal, have been leached by one procedure, varying only in details of sample preparation. The results, which explore particularly the correlations of mineralogy and texture to solution of rock and leaching of uranium, provide a basis for deciding what sort of information is ideally desired from leaching techniques, and how best to obtain it.

The intent here is not so much to report results of a geochemical nature but to outline the theoretical bases and purposes of leaching studies in uranium geochemistry, to dwell briefly on analytical techniques and problems, and to illustrate the type of results to be anticipated and the problems of interpretation by means of a few examples from the work accomplished to date.

It is concluded that the uranium content and leachability of a rock vary nonsystematically from point to point at all scales in an igneous body. This is partly a consequence of the sensitive response of an element present in minute concentrations to slightly changing conditions during crystallization. Superposed are other variations resulting from reactions with natural solvents whose access to contained uranium is erratic and changing. Amounts and fabric distribution of uranium in igneous rocks must thus be related to geologic processes and environments rather than solely to amounts of other elements.

THEORETICAL BASES FOR LEACHING STUDIES

Leaching, an everyday tool of hydrometallurgical research and practice, is a technique that permits discrimination of the different occurrences of an element among the constituents of a rock -- or an ore. Basically, the leaching solvent dissolves certain specific constituents of a rock, while leaving other constituents unaffected. The distribution of uranium between soluble and insoluble constituents of an igneous rock provides information relative to the distribution of uranium in the sample, providing the identity of the soluble and insoluble constituents is known, and further provides an additional set of data bearing on the geochemical history of uranium in the rock under investigation.

In hydrometallurgical practice, leaching is primarily a technique for dissolving those particular minerals that contain the desired element, thus separating ore metal from waste mineral. Such an approach on a laboratory scale can also be of use to geochemical investigations, except that in minor-element studies the element of interest is unlikely to be confined to one or to a few mineral species, but occurs throughout all parts of a rock and in a variety of ways. This being so, it is desirable to design leaching experiments to selectively test different parts of a rock, both textural and mineralogic.

Uranium -- and presumably also other minor elements -- is hypothesized to exist in the fabric of an igneous rock in the following ways (Neuerburg, 1956, p. 58): (1) uranium minerals; (2a) uranium substituting in minor amounts for cations and anions in the structures of rock minerals; (2b) uranium located in minor amounts in structural defects of rock minerals; (3) uranium held in cation-exchange position; (4) uranium adsorbed on crystal surfaces, on surfaces of crystallographic discontinuities, and on surfaces of irregular cracks within crystals; (5) uranium dissolved in fluid inclusions contained within rock minerals; and (6) uranium dissolved in intergranular fluids. On exposure of an igneous rock to a fluid, natural or artificial, with which it may react, uranium in each of the listed occurrences will respond differently. The nature of that response will depend upon the physical-chemical state of uranium in each occurrence, upon the nature of the reactive fluid, upon the physical character of uranium in each occurrence, and upon the textural character of the rock, principally as regards access of the reactive fluid to each part of the rock fabric.

Theoretically, and with full knowledge of the chemical behavior of all the constituents of a rock, it should be possible to design leaching solvents for selectively analyzing the uranium content of each part of a rock, both as to documenting each fabric occurrence and measuring the amount of uranium contained therein. If this prediction is met, leaching techniques may provide a much more accurate means of measuring the uranium contents of mineral species in a rock than the present technique of analyzing mineral separates, which sample only a selected size-fraction of each mineral species in a rock (Neuerburg, 1956, p. 59).

From the viewpoint of geochemical histories of uranium in igneous rocks, it is useful to classify the fabric occurrences of uranium into two parts, each of which has a unique and practical significance in geologic processes. Uranium contained within rock minerals (fabric occurrences 2 and 5) is effectively removed (armored) from reaction with any fluids passing through a rock that do not react with the mineral containing uranium. Uranium minerals and loosely bound uranium (fabric occurrences 1, 3, 4, and 6) are so situated and constituted as to be especially reactive with fluids passing through a rock, insofar as the texture permits attainment of the reactive fluid to their physical sites. Thus, uranium contained in rock minerals represents uranium emplaced in a rock at the time of its crystallization -- or last recrystallization, if a metamorphic or altered rock -- and subsequently preserved, whereas uranium minerals and loosely bound uranium ions (whether emplaced during crystallization or not) represent uranium whose fabric disposition and amount may have been changed since crystallization of the rock. These latter occurrences of uranium are hereinafter termed labile uranium. If precise measurements of labile uranium can be made and its pattern of distribution in rock masses relative to structural and petrographic features determined, information on the past movement of uranium can be obtained and used to evaluate geologic processes and ore forming processes. An analogous situation should hold for other minor elements.

ANALYTICAL TECHNIQUES

The leaching technique used to date in this study is as follows: approximately four grams of rock, pulverized to pass 38 mesh, are leached in 0.05 molar nitric acid on a steam bath at a terminal temperature of 80-85° C for one half hour (200 ml of solvent is used for each gram of rock). The loss of sample weight due to solution is determined. The undissolved residue is taken into solution with a sodium peroxide fusion, and it and the leach solution separately analyzed for uranium, using a fluorimeter of the type designed by the U. S. Geological Survey (Kinser, 1954).

This procedure was arrived at on the basis of preliminary experiments that showed it to entail virtually complete solution of sexi- and quadrivalent uranium minerals, while dissolving no more than 10 percent apatite and less than 5 percent sphene, both sized to plus 100, minus 35 mesh. In practice the procedure dissolves considerably more rock substance than would seem indicated by the preliminary experiments on mineral solubility. By and large, there seems to be little difference in the solubility of most rock types (about 3 percent rock substance), but granitic rocks tend to be somewhat less soluble (about 1 percent) under this procedure and feldspathoidal rocks to be considerably more soluble (from 5 to 20 percent). Rock solubility should be held below 0.1 percent to lend confidence to the interpretation that leachable uranium is substantially equivalent to labile uranium. In part the appreciable rock solubility obtained in this study may be due to the greater reactivity of fine-grain sizes in the unsized sample and to greater solubility than anticipated of some rock minerals, such as hornblende and biotite.

Although the bulk of leaching data obtained with these rock solubilities -- greater than 0.1 percent -- cannot be directly equated with labile uranium, they do illustrate some trends of interest and provide a working basis for designing further experiments on leaching solvents. The "ideal" leaching solvent for the purposes in mind should selectively dissolve uranium minerals and loosely bound uranium ions, but it must not dissolve common rock minerals. Currently, experiments are under way to evaluate carbonate solutions and electrodialysis techniques as possible answers to this problem.

SAMPLING

The matter of sample size and choice deserves some comment here. Because the study is primarily aimed toward relating uranium content and distribution to geologic processes -- by way of correlations with structural environment and petrography -- rather than to rock types or units, special interest has been given to the magnitude of point-to-point variations in uranium content and leachability in both homogeneous and heterogeneous outcrops of igneous rock. Much data in the literature indicate that the uranium content and fabric distribution within rock masses varies considerably; furthermore, such variation is predictable from petrographic observation and from theories regarding minor-element partition during crystallization. Study of the magnitude of point-to-point variation relative to geologic features has encouraged some uncommon sampling procedures, principally the use of small samples, and has yielded one unexpected result.

In the first investigation of this spatial variation, 4-gram splits taken from pairs and triads of approximately 1- to 2-pound hand specimens from apparently homogeneous outcrops were analyzed. Uranium analyses indicated considerable point-to-point variation, but it was soon evident that the variation was unpredictably augmented and decreased by unavoidable losses and rock fractionation occurring during mechanical splitting of material ground to minus 38 mesh.

The next experiment consisted of taking 52 one-centimeter cubes of about 4 grams weight, irregularly distributed throughout a 6-inch cube of noritic anorthosite that is coarse grained and both mineralogically and texturally heterogeneous. The total uranium contents showed unexpectedly small variation (fig. 1), leading to the idea that 4-gram single-fragment samples might generally be adequate samples to measure the uranium contents of igneous rocks, even of such coarse-grained rocks as anorthosite. The use of such small samples is generally desirable because they can be analyzed without need for mechanical splitting, thereby obviating some of the chances for introduction of error from sample handling.

This tentative conclusion finds further support in subsequent investigations of the point-to-point variation among pairs and triads of 4-gram single-fragment samples from hand specimens and from outcrops. The histograms of figure 2 contrast the extent of point-to-point variations so far found (excluding the data of figure 1) among 4-gram fragment samples and among 4-gram samples split from pulverized hand specimens. The variation among the fragment samples is markedly less than that among the split samples.

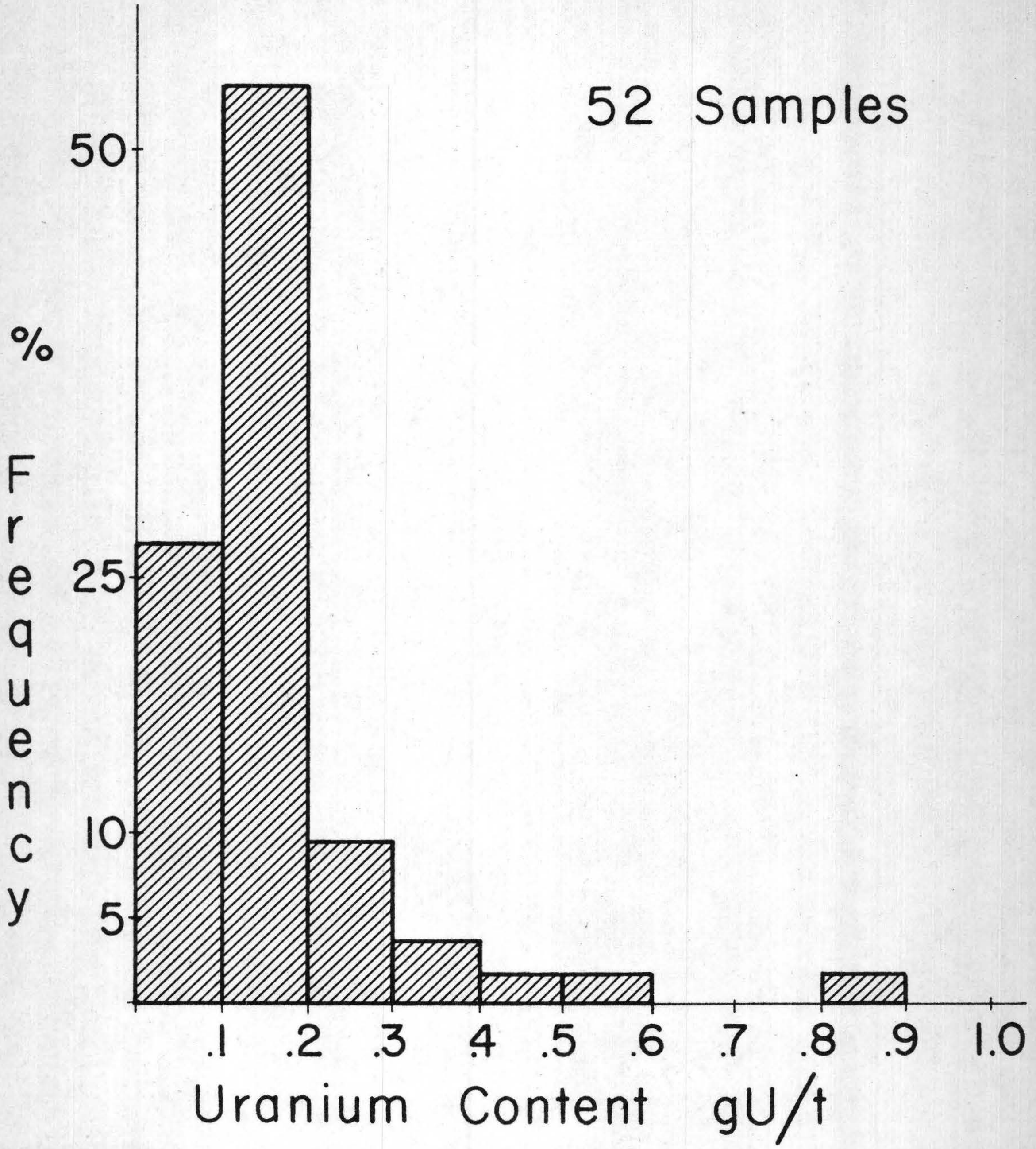

Figure 1. Variation in total uranium content of 1 cm cubes, weighing approximately 4 grams, cut from a 6-inch cube of heterogeneous noritic anorthosite.

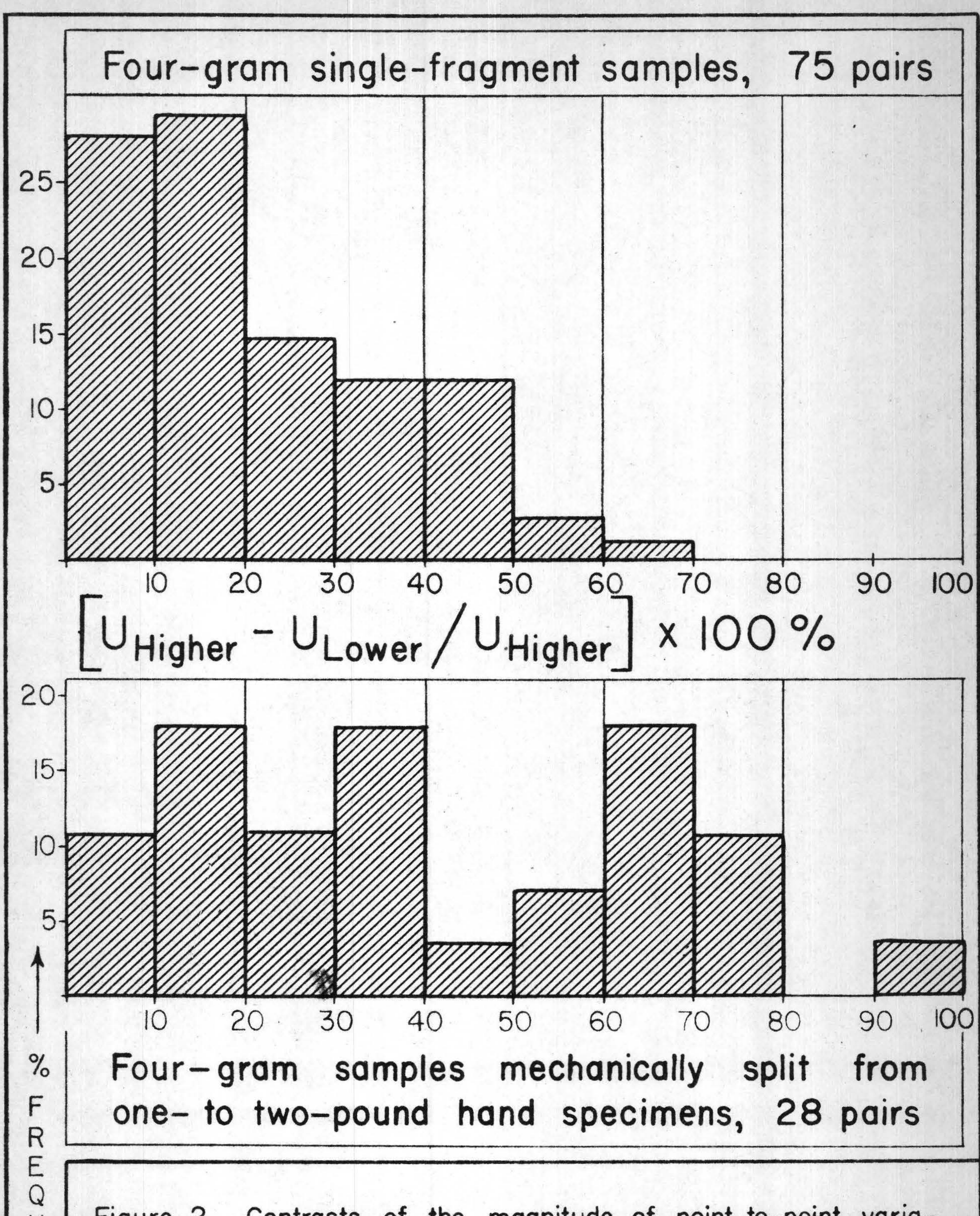

Figure 2. Contrasts of the magnitude of point-to-point variations in total uranium content between samples split from pulverized hand specimens and 4-gram single-fragment samples.

SOME RESULTS OF THE LEACHING STUDIES

A few of the results of the leaching studies to date are reported here, partly to illustrate the problems inherent in the studies and partly to indicate ways in which leaching studies may be useful to geochemical interpretations. Fundamentally, labile uranium may be expected to reflect two major processes in the history of a rock. Initially, it might be expected to reflect rock composition and the finally crystallized minerals as these are controlled by differentiation and by the physical-chemical details of crystallization. Secondly, it is conceivable that labile uranium is controlled in its amount by various agents that have affected a rock since its crystallization.

Because the leaching procedure used here does not, by virtue of its solution of appreciable rock substance, give a true measure or even a relatively comparable estimate -- from rock to rock -- of labile uranium, any generalized relation between labile uranium and rock composition cannot be justifiably construed from the current data. The histograms of figure 3, illustrating the leachability of uranium from several rock types, can only be taken to mean that the distribution of uranium between soluble and insoluble rock substance, using the procedure outlined, is relatively independent of rock type.

That the relative proportion of labile uranium can correlate with rock composition is indicated by the decrease in leachable uranium in the differentiation sequence of the diabase that intrudes the Apache group of Precambrian age in Gila County, Arizona. Both the total uranium content (fig. 4) and such effective uranium scavengers as zircon and allanite increase in the differentiation sequence from diabase to aplite. On this basis, the correlation of leachable uranium with rock composition is considered to result from an increasing incorporation of a greater percent of

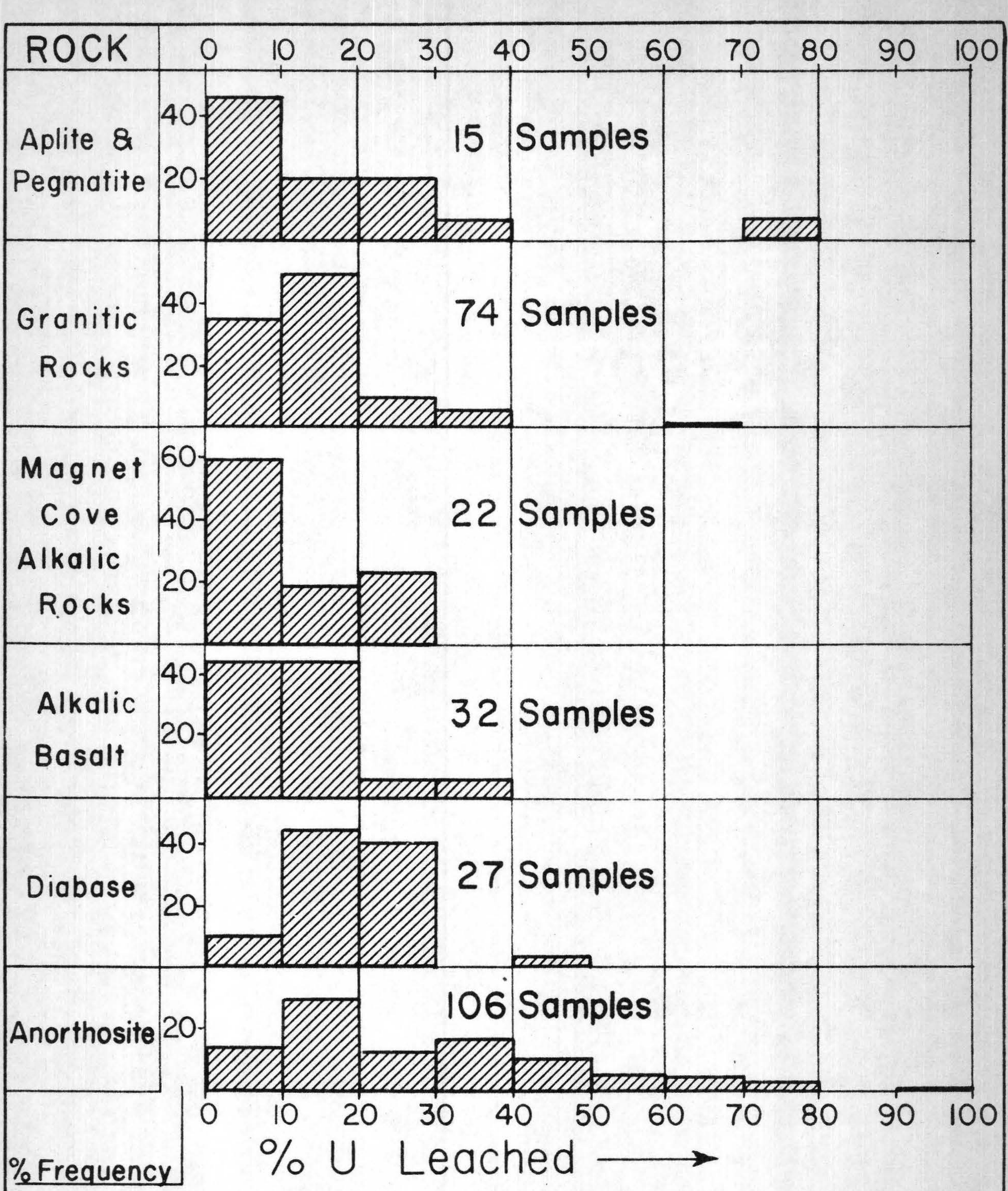

Figure 3. Leachability of uranium from several rock types in 0.05-molar nitric acid.

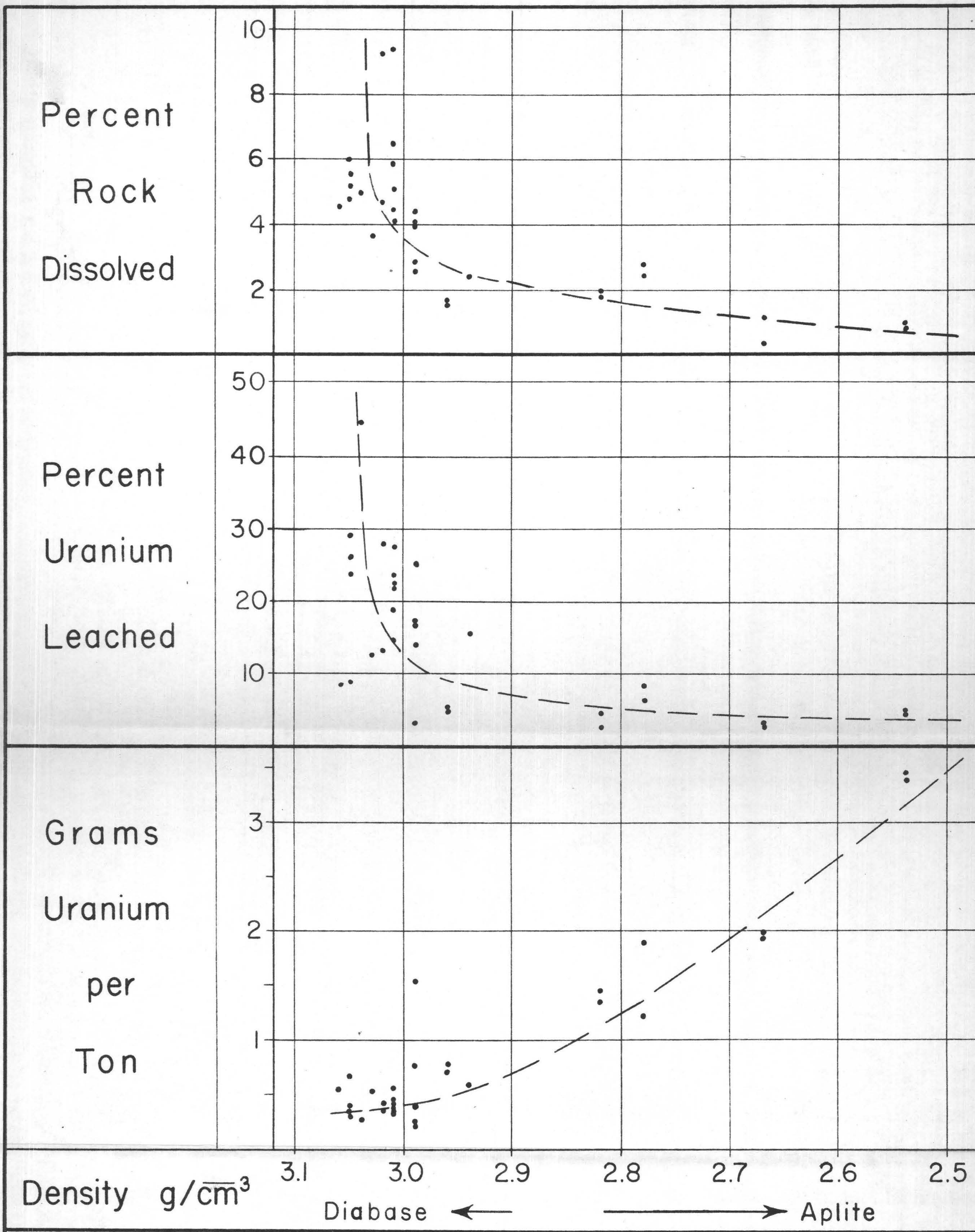

Figure 4. Trends of total uranium content, uranium leachability, and rock solubility in the differentiation sequence of the diabase that intrudes the Apache group, from diabase to aplite. 31 samples.

the total uranium present into insoluble minerals (fig. 4) as both the uranium concentration of the magma and the amount of uranium scavengers increased.

Although all analyses made thus far indicate no emphatically characteristic uranium contents with respect to rock type, generally characteristic ranges of uranium contents are indicated for some of the gross rock types (fig. 5); for example, few anorthosites have more than one gram of uranium per ton but most granites contain a few grams of uranium per ton. Theories of minor-element partition during crystallization (e.g., Neumann et. al., 1954) indicate that the concentration of uranium in a magma should have a major control on the final proportions of labile uranium. Thus, the total uranium concentration of a rock specimen may provide a more fundamental correlation with the amount of labile uranium than does the composition of the rock specimen. The histograms of figure 6, wherein leachable uranium is plotted in terms of orders of magnitude concentration of uranium, indicate that this is possibly the case -- as an inverse relation. However, these data should be viewed with caution for it is possible that the indicated correlation may be related to a decrease in analytical precision as total uranium concentration decreases.

Investigations of labile and total uranium contents relative to geologic features or processes proved to be frequently frustrated by one characteristic of the occurrence of uranium in igneous rocks: that is, the point-to-point variation in uranium content, whether original in crystallization or secondary in the post-crystallization history of the rock. In many experiments, the point-to-point variation (a reflection of many variables) was found to be so large as to exceed any changes that might reflect a particular geologic process. Thus, the "background noise" level of this variation prohibited detection of any change in uranium

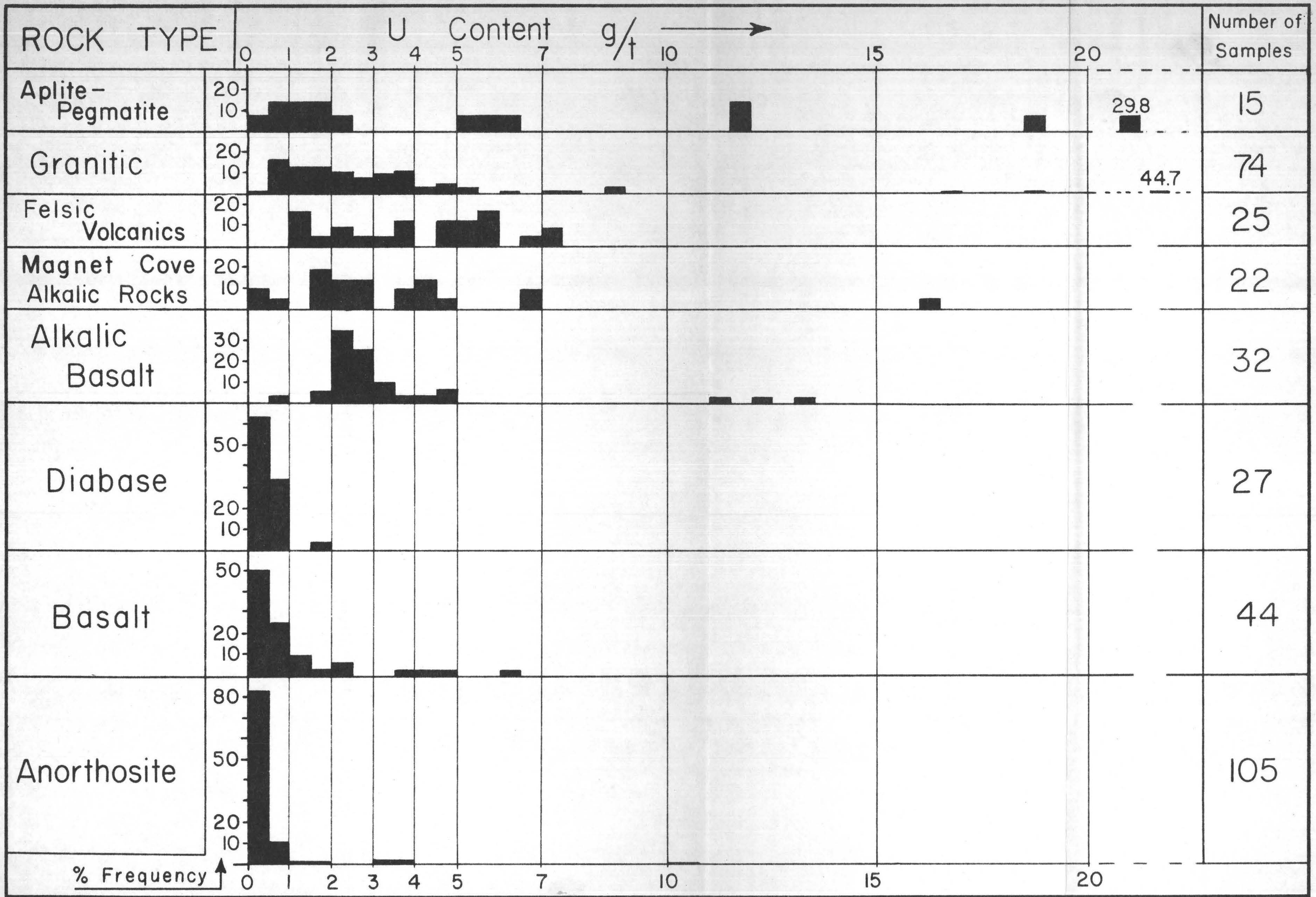

Figure 5. Frequency of total uranium contents among several rock types.

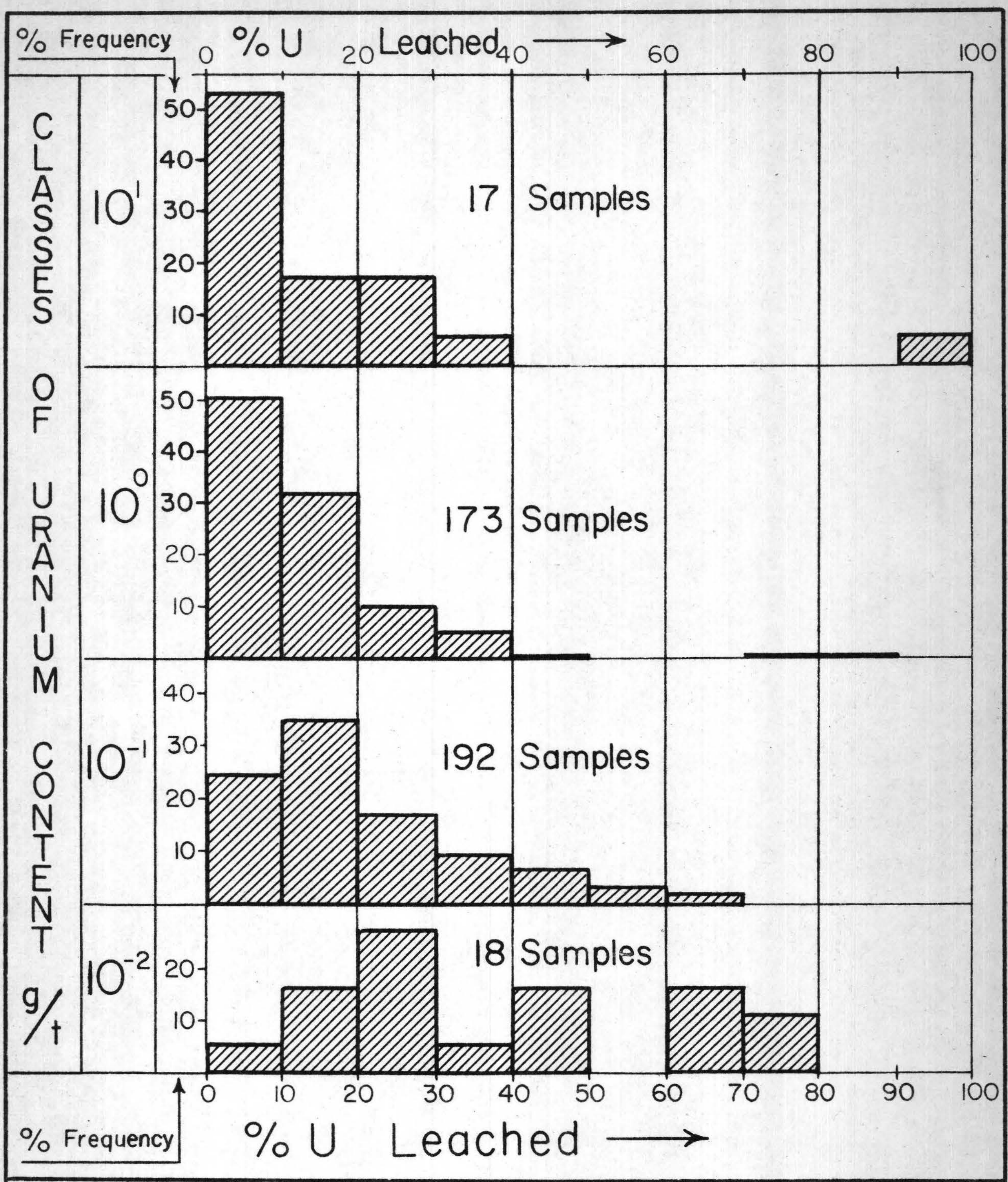

Figure 6. Leachability of uranium from a variety of igneous rocks in 0.05-molar nitric acid relative to orders of magnitude concentration of total uranium.

content and leachability relative to depth (such as that suggested by Hurley, 1950, p. 5) in three sets of cores from the Laramie Range, Wyoming, the Front Range, Colorado, and Butte, Montana. This is well illustrated by the Butte section (fig. 7), where the variation of leachable and total uranium is fully as great at a single depth as between different depths. The same difficulty cropped up in investigations of the effects of progressive metamorphism and of weathering on both total and leachable uranium contents of igneous rocks.

An extensive study has been initiated on the geochemical history of uranium in the diabase in the Apache group and of the relation of spatially associated uranium ore deposits to the diabase, relying upon measurements of leachable uranium to resolve some geochemical uncertainties. The uranium content of chilled selvages on several of the diabase sills is greater than the uranium content of the diabase of the sills. Whether this higher concentration is an original feature -- i.e., a measure of the magmatic uranium concentration -- or is a result of later solutions whose movement has been guided by intrusive contacts is a critical phase of this study. A number of samples were taken along a traverse through part of one sill, across its chilled contact, and outward along a bed in the intruded sedimentary rocks. The uniformity in amount of leachable uranium contents across this contact (fig. 8) indicates no introduction or movement of uranium since crystallization and thus provides evidence for the contention that total uranium in the chilled selvage reflects the minimum uranium content of the diabase magma.

The behavior of leachable uranium across the diabase intrusive contact and in the differentiation sequence of the diabase is taken as evidence that the uranium contents of the different rocks of the diabase sills that intrude the Apache group are unchanged since crystallization was completed.

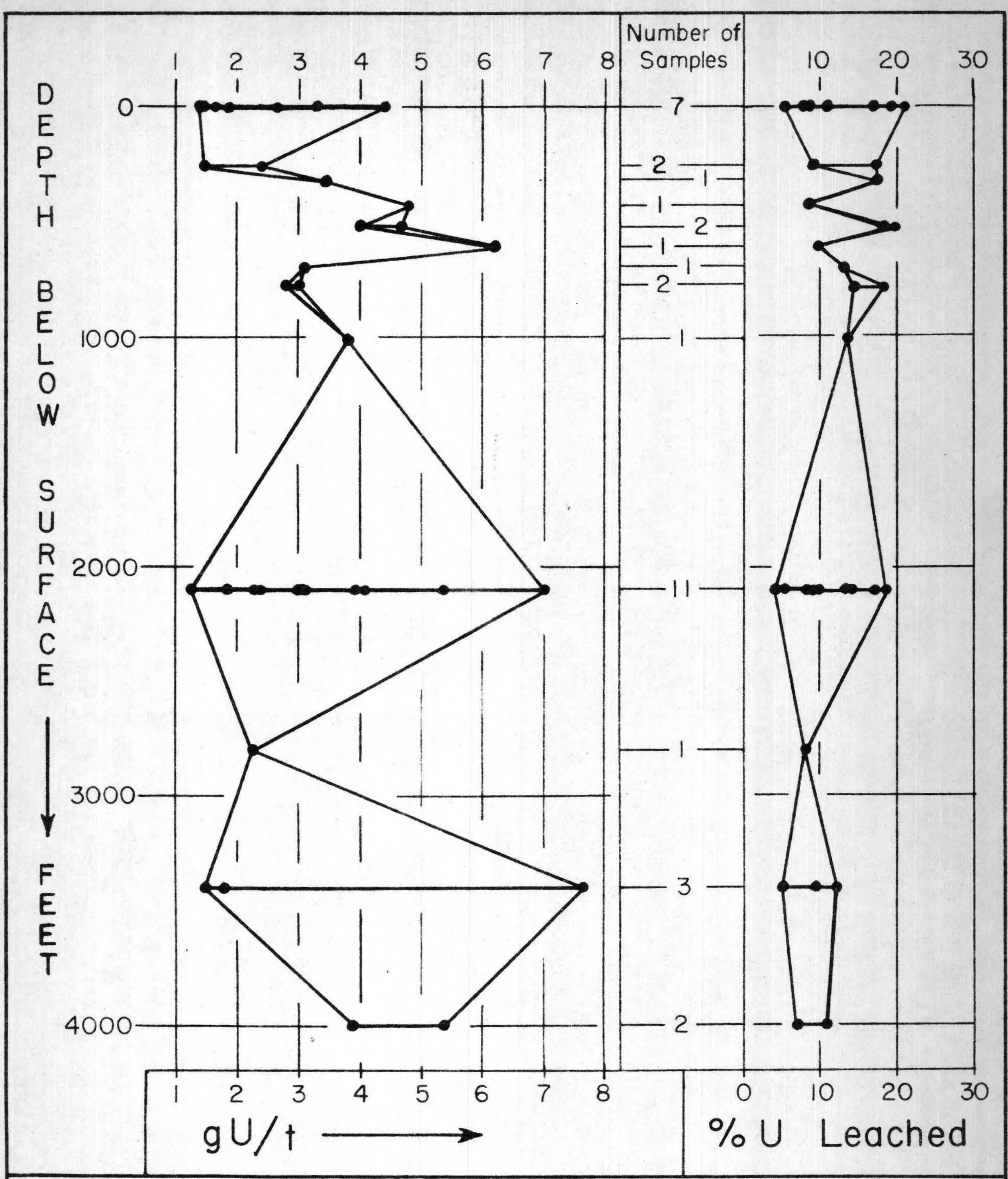

Figure 7. Variations in total and leachable uranium contents of quartz monzonite at single depths and with depth at Butte, Montana.

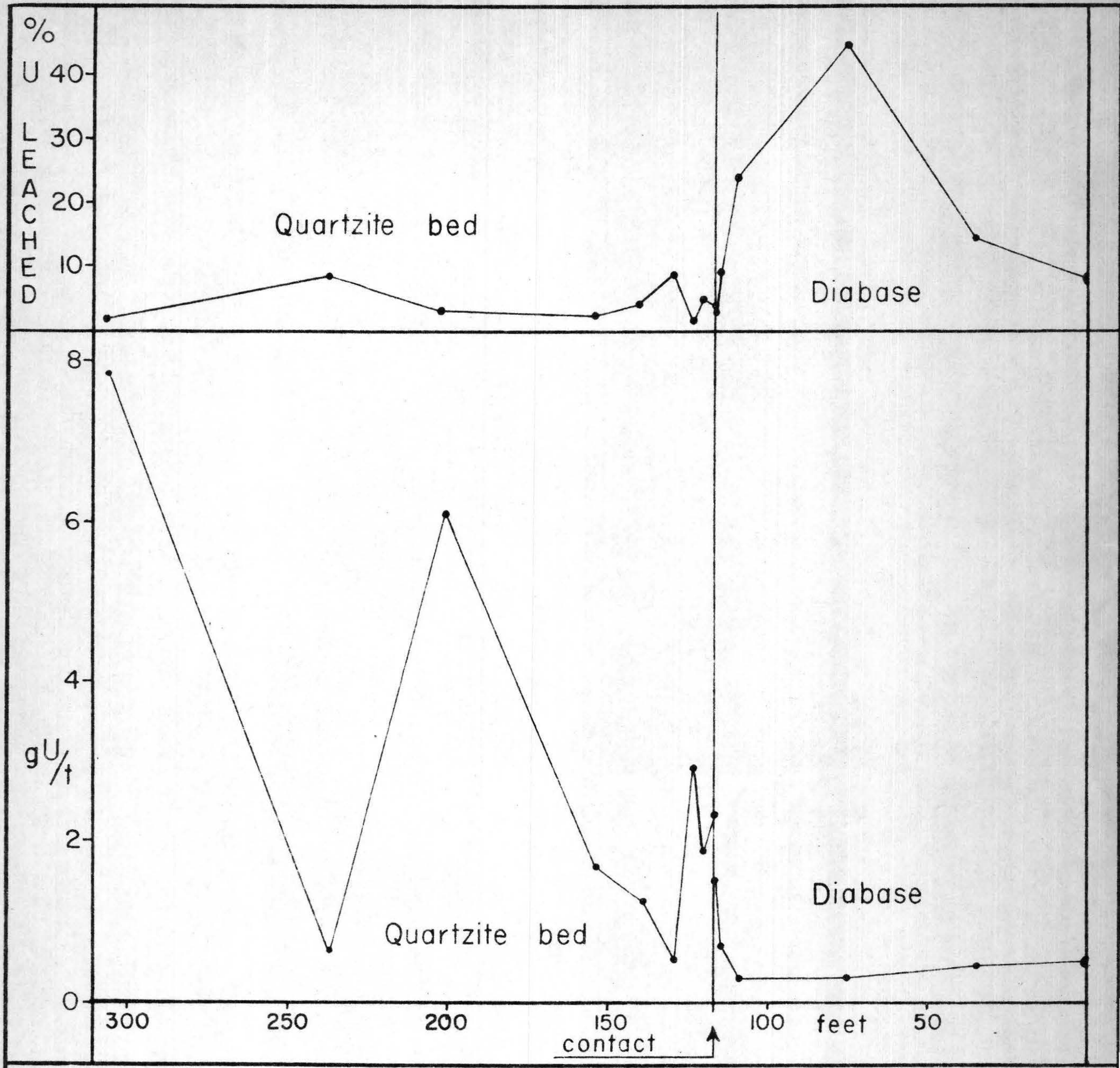

Figure 8. Changes in total and leachable uranium contents across a contact of the diabase that intrudes the Apache group with the Dripping Spring quartzite, Gila County, Arizona.

Using the total uranium contents of the chilled selvages as a measure of the original total uranium content of the diabase magma and contrasting this against the observed uranium contents of the differentiation products according to their respective specific gravities and volumetric abundances, it is calculated that on the order of 1,000 metric tons of uranium metal per cubic kilometer of diabase has been lost from the major diabase system in the Apache group during its crystallization. This loss encourages the possibility that the diabase may be the source of uranium in the associated ore deposits.

In emphasis: the behavior of leachable uranium relative to total uranium, petrography, and structural environment may indicate whether the total uranium content of a rock is original with crystallization or subsequently changed. This apprcach may provide a method for identifying intrusives potentially the source of metals in ore deposits in the fashion just illustrated. More work is in progress to further test the validity of these tentative conclusions, but the point here is made of the usefulness and importance of leaching studies in the diabase experiment and in similar experiments.

CONCLUSIONS

The present progress report of leaching studies of a number of igneous rocks has been offered as an argument in favor of using leaching studies as an important tool in extending knowledge of the geochemistry of uranium in igneous rocks. The basic premise of leaching techniques as a means of measuring uranium in its different fabric occurrences in an igneous rock has been briefly explained, and some of the analytical problems listed. The results illustrating the problems encountered and the nature of some of the results obtained serve to outline the profits that can be expected from leaching studies, especially as these relate to geochemical processes determining the crustal distribution of uranium.

ACKNOWLEDGMENTS

The cooperation of the Anaconda Company in providing specimens from their properties at Butte, Montana, is gratefully acknowledged. This work was done by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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