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Water Contents of Samples from the Nevada Test Site: Total, Free (Natural State to 105°C), and More Tightly Bonded (105–700°C)

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ABSTRACT

To help confirm correct functioning of an epithermal neutron sonde, we measured tightly bonded water content of selected Nevada Test Site (NTS) drill holes. Tuff and alluvium samples were dried overnight at 105°C. The samples were then heated for 45 min in a split tube furnace at 700°C. The water that came off due to this heating was collected and the amount recorded. The error in this procedure is ±0.59 wt%.

Total water can be calculated for samples from analyses of free and tightly bonded water contents. The maximum error in this calculation is equivalent to the error in determining the more tightly bonded water.

Average total water content values have been assigned to geologic units. These values, in weight fraction, are alluvium 0.14 ± .05 and tuff 0.19 ± .04. Further division of the tuff gives values of Rainier Mesa 0.15 ± .01, Paintbrush 0.18 ± .03, Tunnel Beds 0.20 ± .04, and Grouse Canyon 0.29 ± .02. Statistically significant differences occur between the tuff and alluvium. Within the tuffs, these differences also occur between Grouse Canyon, Rainier Mesa, and Paintbrush/Tunnel Beds. Paintbrush and Tunnel Beds cannot be distinguished by this method.

INTRODUCTION

It is important accurately to determine water content of the rock media at Nevada Test Site in order to predict the phenomenology of underground nuclear explosions. Currently, water content is determined by promptly canning Hunt sidewall samples at the drill site and later measuring water content.

Total water content is the water in the pores between the mineral grains (interstitial water) and water contained within the minerals of the rock (in the chemical structure). Water associated with rock is classified as free (loosely held) or bound (tightly held). Temperature ranges for various types of free and bound water are listed in Table 1. These temperature ranges are from thermal gravimetric and infrared studies on zeolitic tuffs from NTS (Knowlton and McKague, 1976).

In the petroleum industry, a neutron log is used to measure total water content in *saturated* rocks. The tool actually measures hydrogen content of the drill hole wall. If there is no extraneous hydrogen in the area, these measurements indicate the water content of the surrounding rock and are quite satisfactory. The possibility exists, though, that there are sources of hydrogen other than total water as defined in the preceding paragraph. Water exists in cracks and fractures. This kind of water will not be part of the canned sample. Other hydrogen compounds found at NTS—hydrogen sulfide, for example—will affect the neutron log. Generally, the neutron log will indicate total water content of the rock media.

Utilization of an epithermal neutron log to measure total water content at NTS would give more continuous data and would be considerably less expensive than discrete sidewall sampling. However, the sonde would have to be calibrated for the *partially saturated* rocks that compose NTS. LLNL has begun to develop such a facility (Hearst, 1978).

TABLE 1. Temperature range at which various classes of water are lost.[a]

Type of water	Description of water	Temperature (°C)[b]
Free water		
Adsorbed water	Surface water held by ion-dipole interaction, generally very loosely bound.	25–90
Zeolite water	Water molecules occupying random positions in cavities and channels within the crystal framework of zeolites.	70–300
Interlayer water	Water molecules occupying random positions between crystal layers in layered silicates such as montmorillonite.	70–300
Bound water		
Coordinated water	Water bound to cations in crystal lattice by coordinate covalent bonding.	200–700+
Anion water	Water bound to lattice anions by hydrogen bonding.	Not determined
Lattice water	Water in the form of hydroxyl groups ionically bonded in definite lattice positions.	200–700+

[a]Adapted from Knowlton and McKague, 1976.

[b]Determined in N_2 atmosphere or in vacuum.

In order to confirm the correct functioning of the sonde, total water content was measured in the laboratory of samples from holes in which the epithermal neutron log had been run. This total water content was determined by measuring different types of water from different splits of the sample. The first measurement, free water, is routinely measured on every sidewall sample at LLNL–Nevada (Ramspott and Howard, 1975). The difference in weight of the sample before (natural state) and after heating to 105°C is considered free water. This difference reflects mainly adsorbed water, but also consists of some zeolite and interlayer water. The second measurement is of more tightly bonded water lost in the 105–700°C temperature range. These measurements have been done at LLNL-Livermore. The loss represents mainly zeolite and interlayer water, but also includes bound waters. It is assumed that all water that will have a major effect on the phenomenology of underground nuclear explosions is removed by heating to 700°C (McKague, 1981).

From the values of free and more tightly bonded water, total water contents were computed. Further studies will show if the values determined by the epithermal neutron sonde are equivalent to corresponding laboratory measurements.

METHOD

SAMPLES AND SAMPLE PREPARATION FOR MORE TIGHTLY BONDED WATER

Between June 21, 1979 and August 28, 1980, 374 NTS samples were tested for more tightly bonded water content. The samples were selected from various depths of the following twelve drill holes: Ue2ep (38), U2ep (32), U2eq (9), U2fc (80), Ue4ah (12), Ue5n (16), U9cn (5), U9cq (40), Ue10bd (16), Ue10bf (28), and U10bg (26). These tuff and alluvial

samples were mainly Hunt sidewall samples with a few horizontal sidewall samples. All samples were pulverized. Sieving revealed grain sizes (in microns) of 150 (35%), 106 (15%), 63 (25%), 53 (10%), 38 (10%), and <38 (5%).

PROCEDURE FOR MORE TIGHTLY BONDED WATER DETERMINATION

Ten samples were designated standards and were used to establish a procedure for determining more tightly bonded water. Preliminary tests indicated that approximately 10 g of sample in one porcelain combustion boat (sample receptacle) dried at 700°C for 45 min was sufficient to determine the more tightly bonded water content. Early tests, however, showed a great deal of fluctuation in the amount of water gathered and it was decided that humidity affected the samples more than expected. In later tests the samples and boats were dried overnight at 105°C in a gravity convection oven. This procedure guaranteed that further tests would measure only the more tightly bonded water.

Each hole had at least one control sample that was run at the beginning and end of the day to provide a daily test of the reliability of the data. Only when there was insufficient bulk sample was no control used (Ue4ah).

Arrangement of the equipment used is shown in Fig. 1. A boat was tared, sample was added to the boat, and the boat reweighed. In order to eliminate humidity effects samples were not prepared in advance. The boat, with sample, was placed in a quartz tube located in a Lundberg split tube furnace. A slight flow of helium or argon gas through the system ensured movement of the volatile H_2O as the sample was heated. The gas passed through a drying tube filled with anhydrous magnesium perchlorate [$Mg(ClO_4)_2$] in order to remove any H_2O or hydrogen associated with it before entering the quartz tube. The water driven off the sample was collected in a weighed Stetser Norton bottle filled with anhydrous magnesium perchlorate. A short piece of rubber tubing ran from the bottle to a beaker of water. Bubbles indicated that the gas was flowing adequately to carry the volatile water. At the end of the run, the bottle was reweighed and the change in weight was recorded.

Since other volatiles (CO_2, H_2S, Cl) are evolved at high temperatures, it was necessary to actually collect this more tightly bonded water to determine its quantity. It is important to note that this method was not used for determination of water content at 105°C. It is assumed that the volatiles are bound

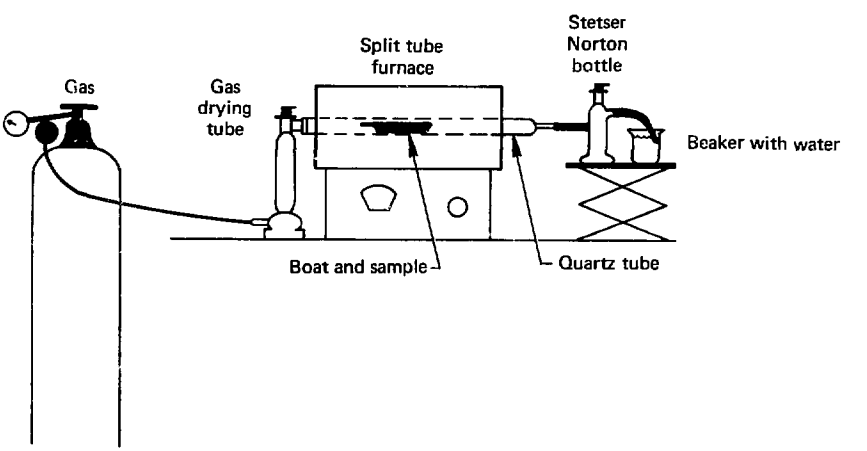

FIG. 1. Arrangement of equipment for more tightly bonded water determination.

tightly to the crystal structure, and are not removed at 105°C. This assumption implies that the sample weight loss at 105°C is entirely water.

ERROR IN MORE TIGHTLY BONDED WATER DETERMINATION

Standard deviation of the weight percent of the more tightly bonded water was determined using data from the above listed samples run three or more times. In all, 113 determinations were obtained from 20 individual samples. Indeterminate error was assumed to be the same for all sample runs, which permitted pooling of the data and calculation of an experimental standard deviation (s) using Eq. (1),

$$s_{\text{more tightly bonded water}} = \sqrt{\frac{\sum_{i=1}^{N_1}(X_i - \bar{X}_1)^2 + \sum_{i=1}^{N_2}(X_i - \bar{X}_2)^2 + \ldots + \sum_{i=1}^{N_k}(X_i - \bar{X}_k)^2}{N - k}} \qquad (1)$$

where X_1, X_2,..., X_k are means of the analysis of k samples, and N ($N_1 + N_2 + \ldots + N_k$) is the total number of measurements made.

From Eq. (1), experimental standard deviation for the determination of more tightly bonded water was equal to ±0.0059 weight fraction.

CALCULATIONS FOR TOTAL WATER CONTENT

It would seem that simply adding the fractional amounts of free and more tightly bonded water would give total water content, but this is not the case. These samples are splits from one original sample, tested at different times for different types of water. Both amounts of water need to be related to the same state, i.e., natural state. Equation (2), developed by Hearst (1980), takes into account wet and dry weights of both sets of samples. It determines total water content of the sample, in the natural state, in terms of weight fraction water:

$$\left(\frac{W^l_{H_2O}}{W^l_D} + \frac{W^7_{H_2O}}{W^7_W}\right)\frac{W^l_D}{W^l_W} = \text{total weight fraction water.} \qquad (2)$$

where

$W^l_{H_2O}$ = weight of water driven off at 105°C (free water),

W^l_D = weight of sample after drying at 105°C,

$W^7_{H_2O}$ = weight of water driven off at 700°C (more tightly bonded water),

W^7_W = weight of previously dried sample to be heated to 700°C,

W^l_W = weight of sample to be heated to 105°C (natural state).

First-order error analysis of Eq. (2) indicates that the error in the more tightly bonded water is by far the largest contributor to the error in total water content. The error in total water content then becomes

$$\frac{W^l_D}{W^l_W} = s_{\text{more tightly bonded water}} = s_{\text{total water}}. \qquad (3)$$

The ratio W^l_D/W^l_W typically ranges between 0.80 ± .0017 and 0.90 ± .0053. Thus, the largest amount of error possible would be the error in the more tightly bonded water (0.0059 weight fraction).

RESULTS

DISTRIBUTION OF VARIOUS TYPES OF WATER IN THE SAMPLES

Figures 2 through 13 show free, more tightly bonded and total water contents and their relationships for each hole. Free water typically makes up 60–90% of the total water content. As expected, free water correlates well with total water content—as total water increases, free water does also, and *vice versa*. The more tightly bonded water can also be correlated to total water content, but not as consistently. More tightly bonded water is 2-33% of the total water content.

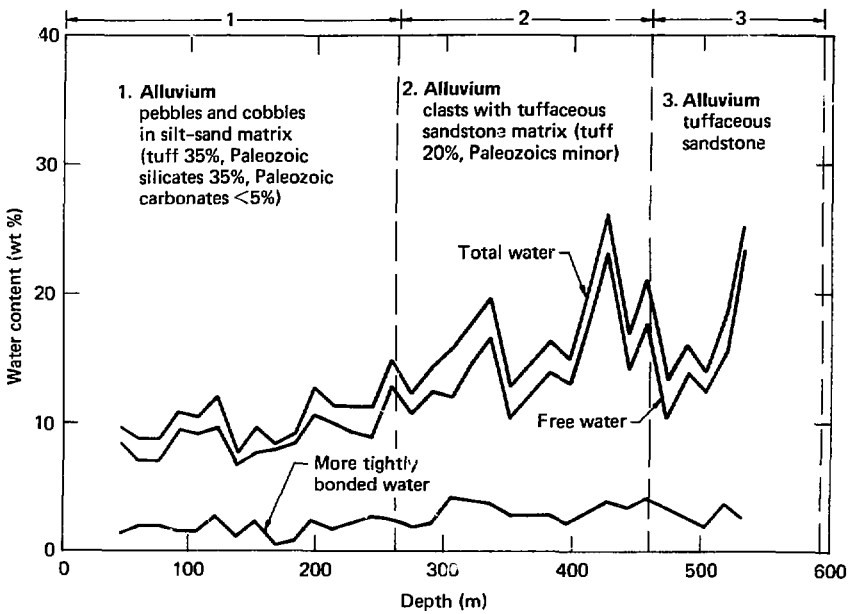

FIG. 2. Laboratory-determined water contents for U2ep, NTS.

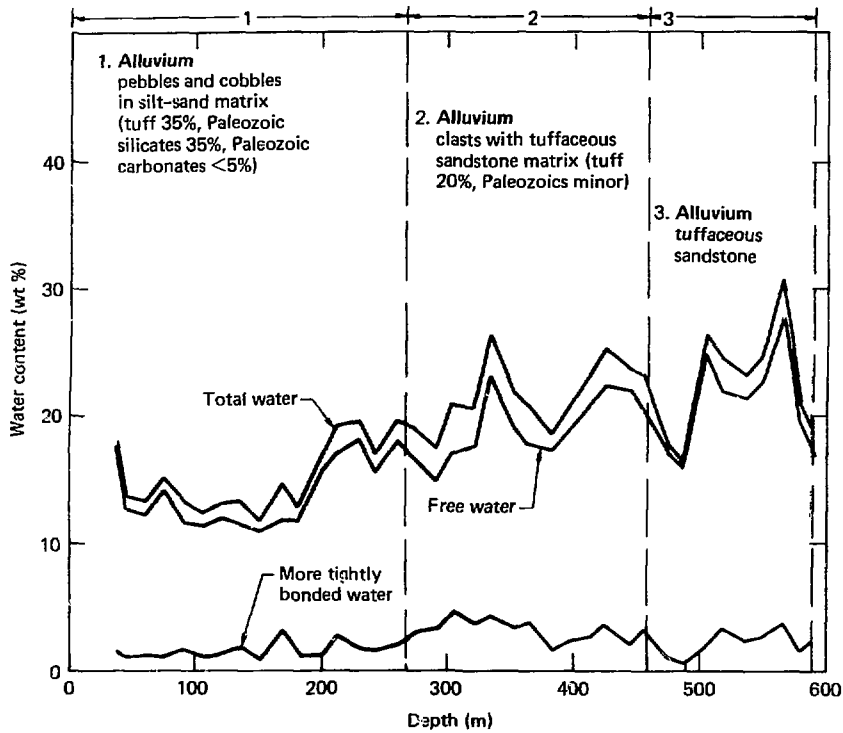

FIG. 3. Laboratory-determined water contents for Ue2ep, NTS.

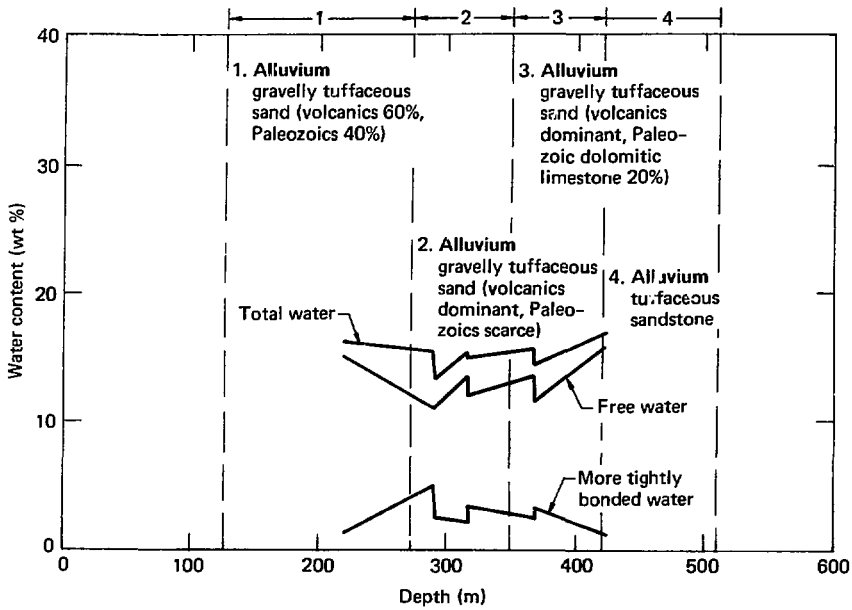

FIG. 4. Laboratory-determined water contents for U2eq, NTS.

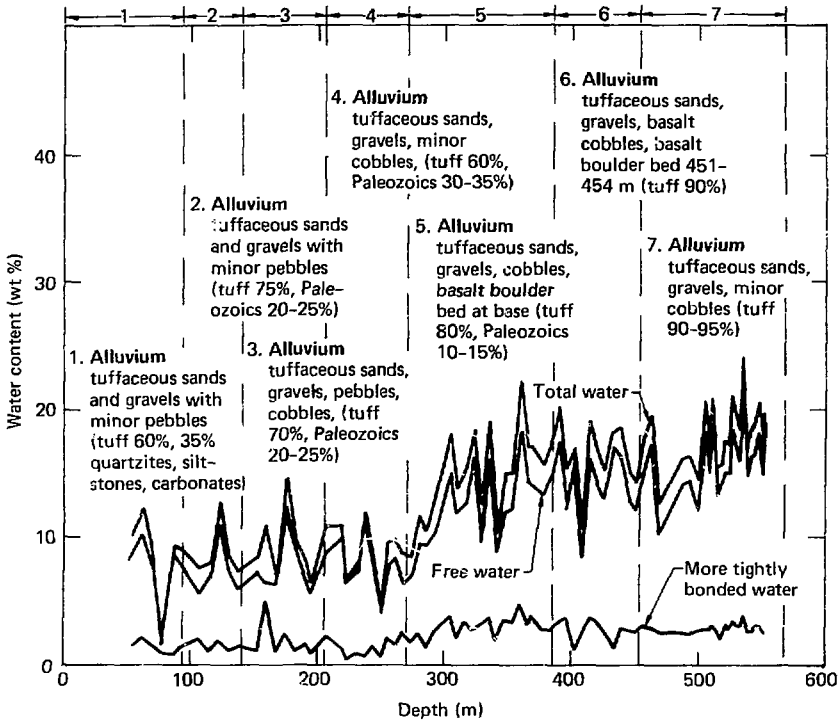

FIG. 5. Laboratory-determined water contents for U2fc, NTS.

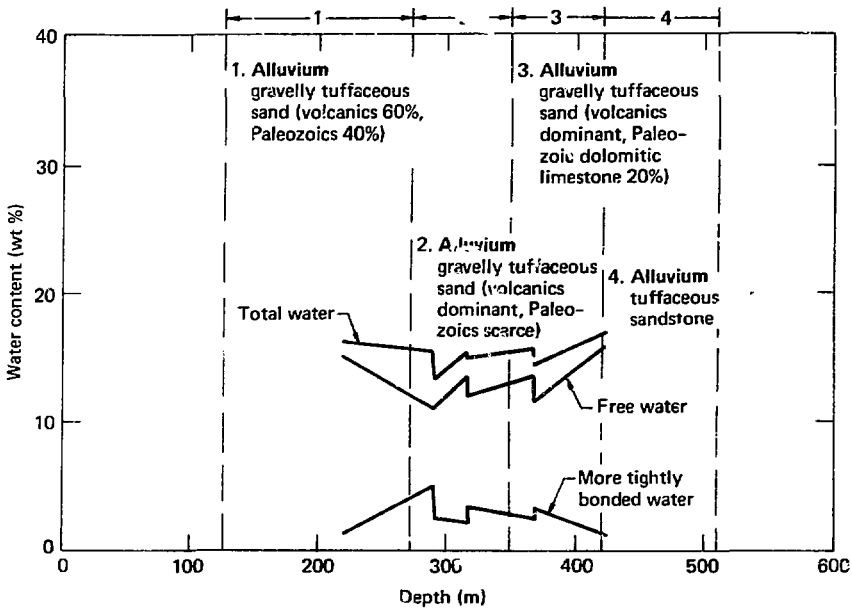

FIG. 4. Laboratory-determined water contents for U2eq, NTS.

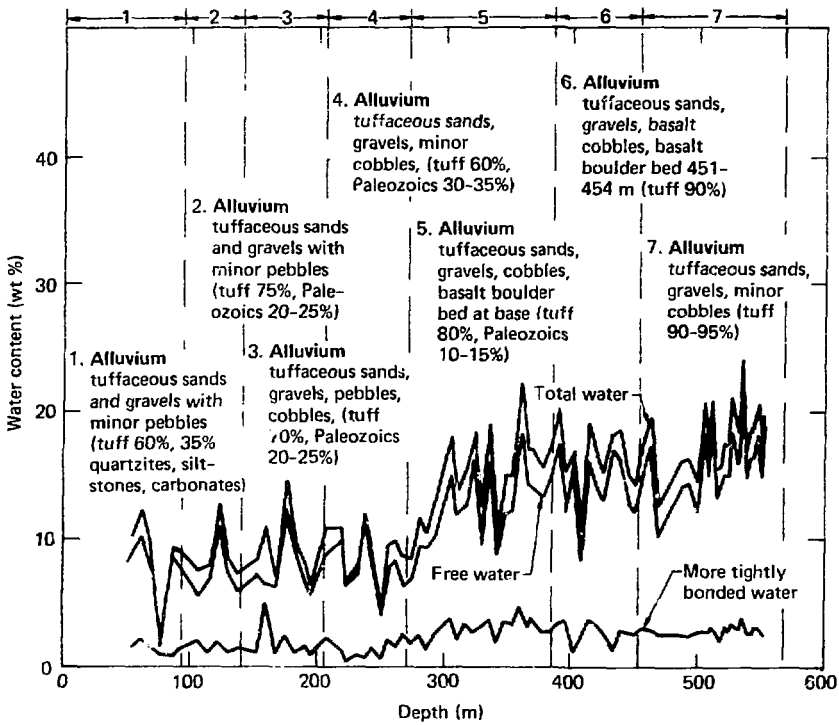

FIG. 5. Laboratory-determined water contents for U2fc, NTS.

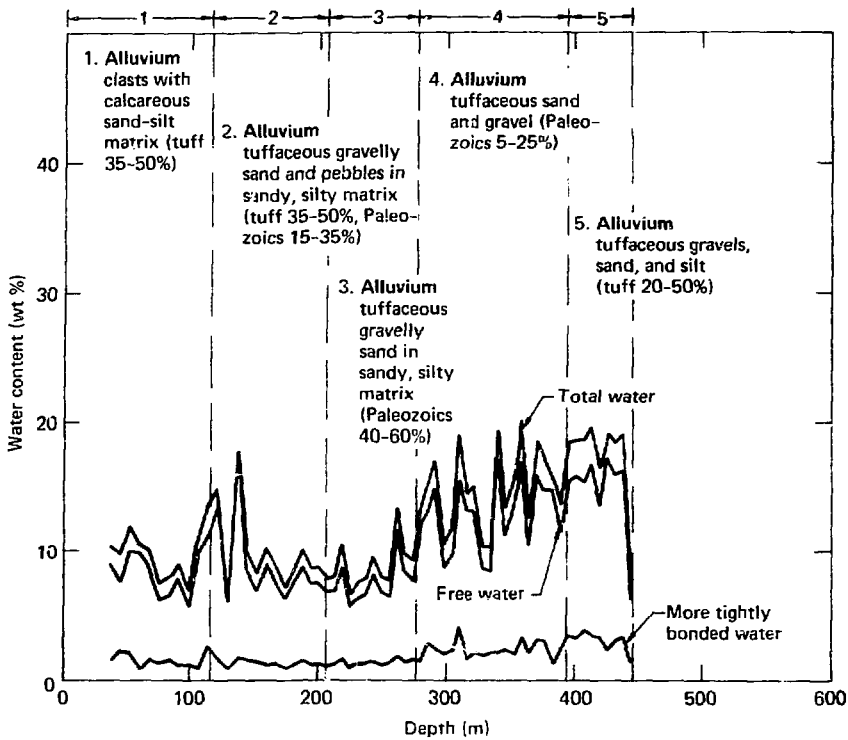

FIG. 6. Laboratory-determined water contents for U2fe, NTS.

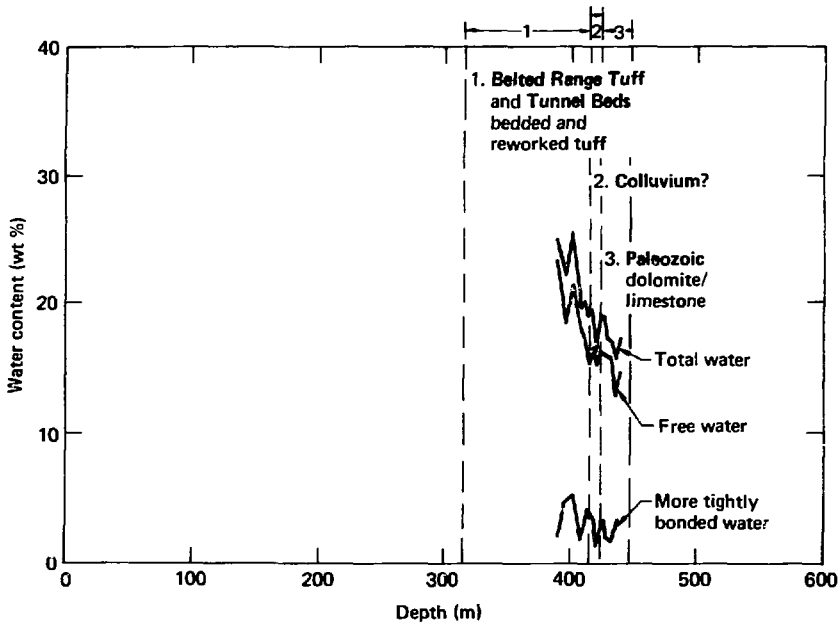

FIG. 7. Laboratory-determined water contents for Ue4ah, NTS.

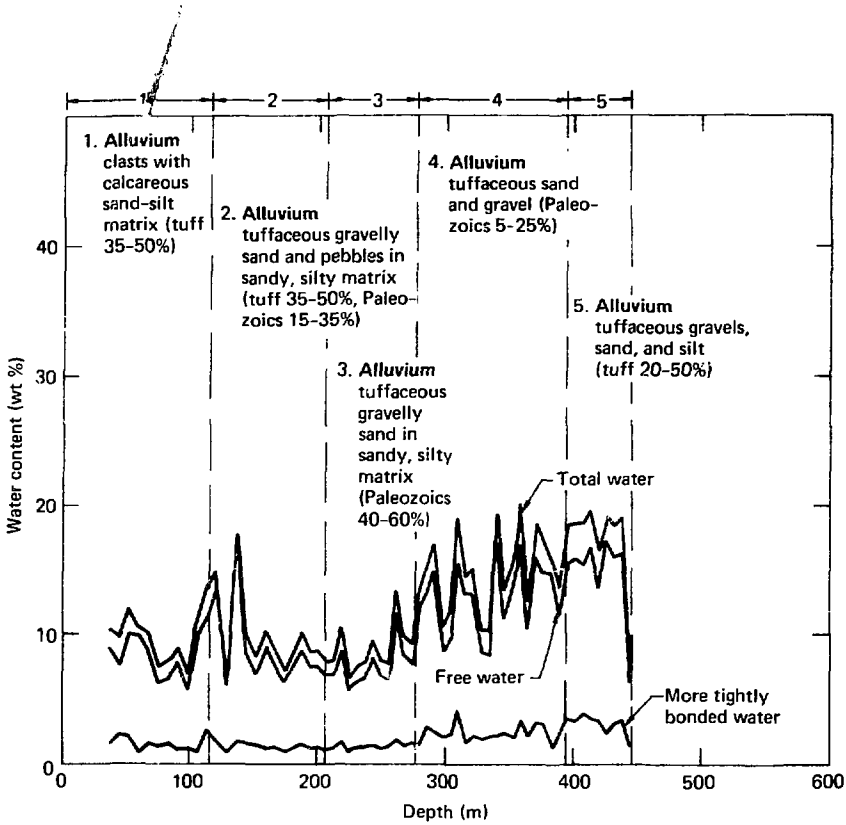

FIG. 6. Laboratory-determined water contents for U2fe, NTS.

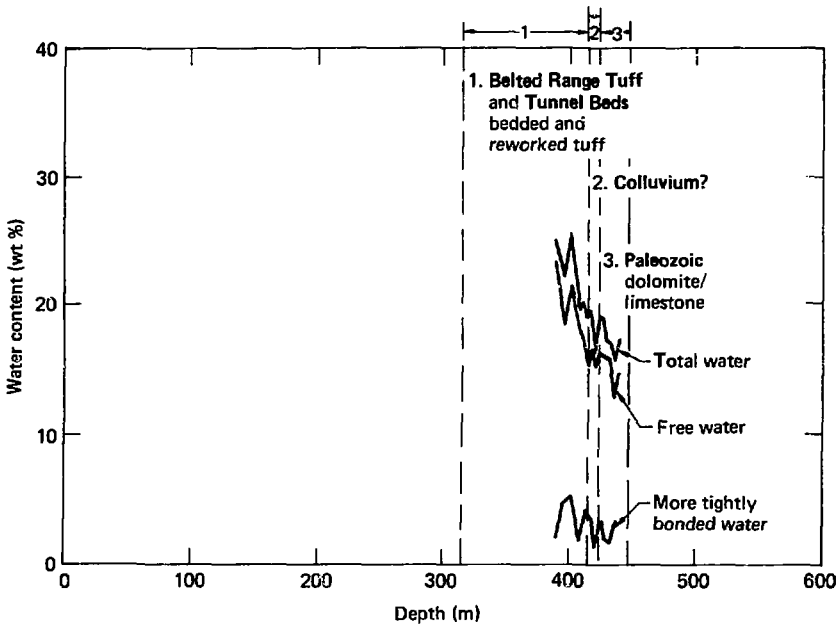

FIG. 7. Laboratory-determined water contents for Ue4ah, NTS.

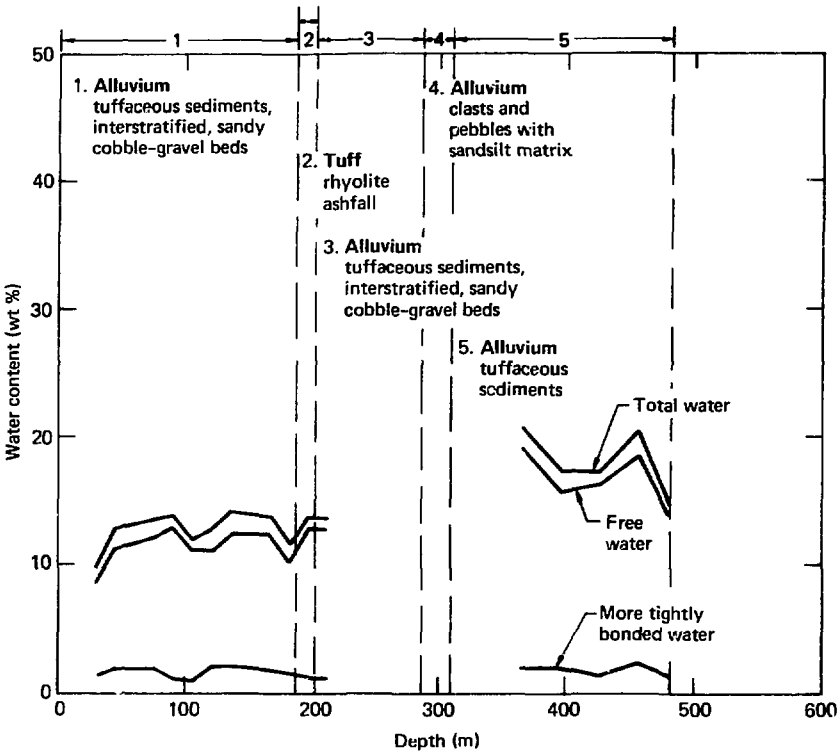

FIG. 8. Laboratory-determined water contents for Ue5n, NTS.

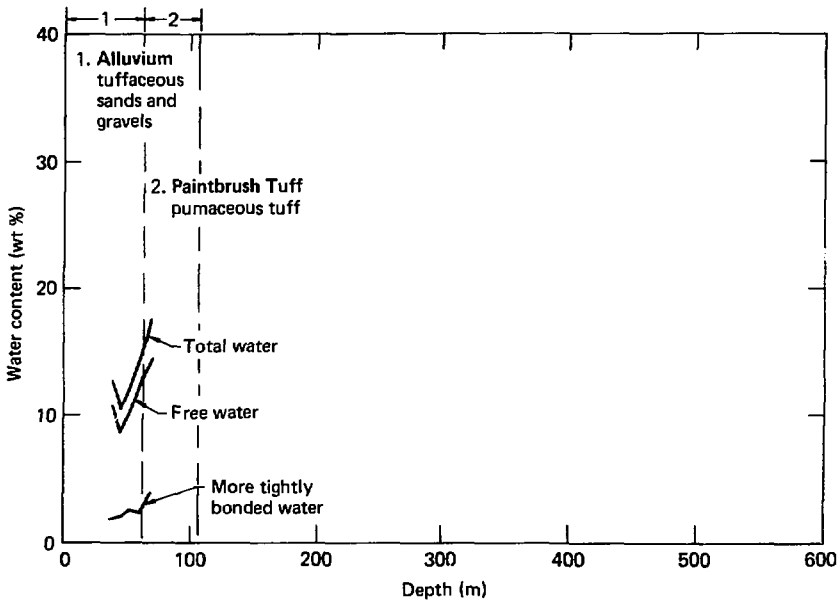

FIG. 9. Laboratory-determined water contents for U9cn, NTS.

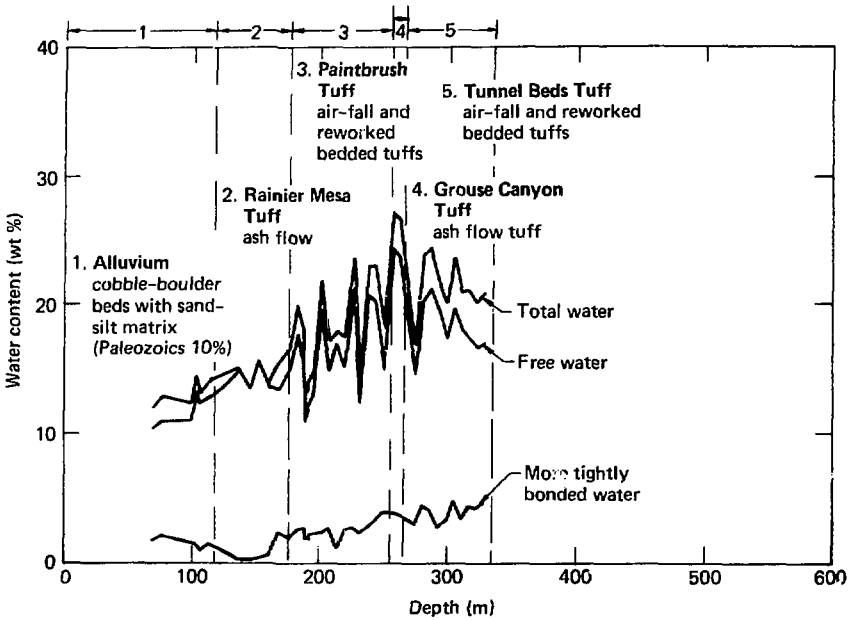

FIG. 10. **Laboratory-determined water contents for U9cq, NTS.**

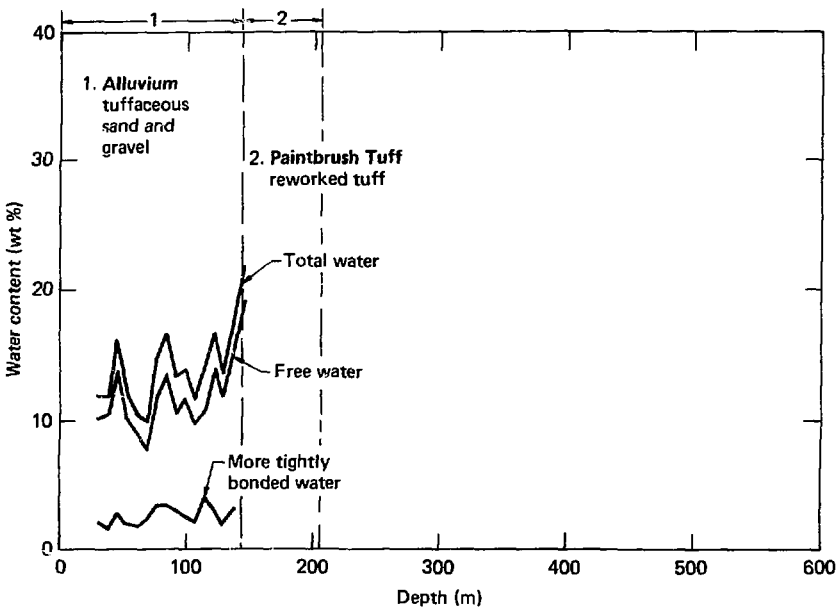

FIG. 11. Laboratory-determined water contents for Ue10bd, NTS.

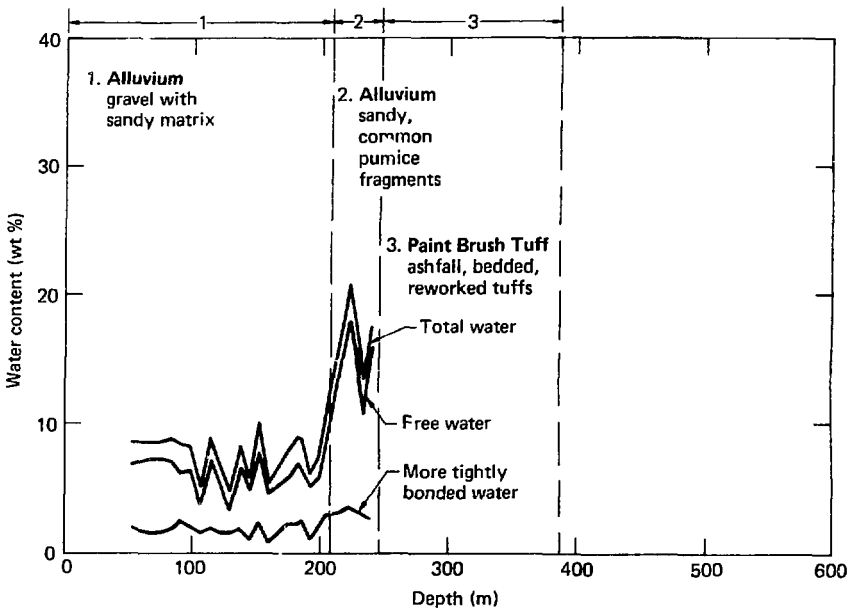

FIG. 12. Laboratory-determined water contents for Ue10bf, NTS.

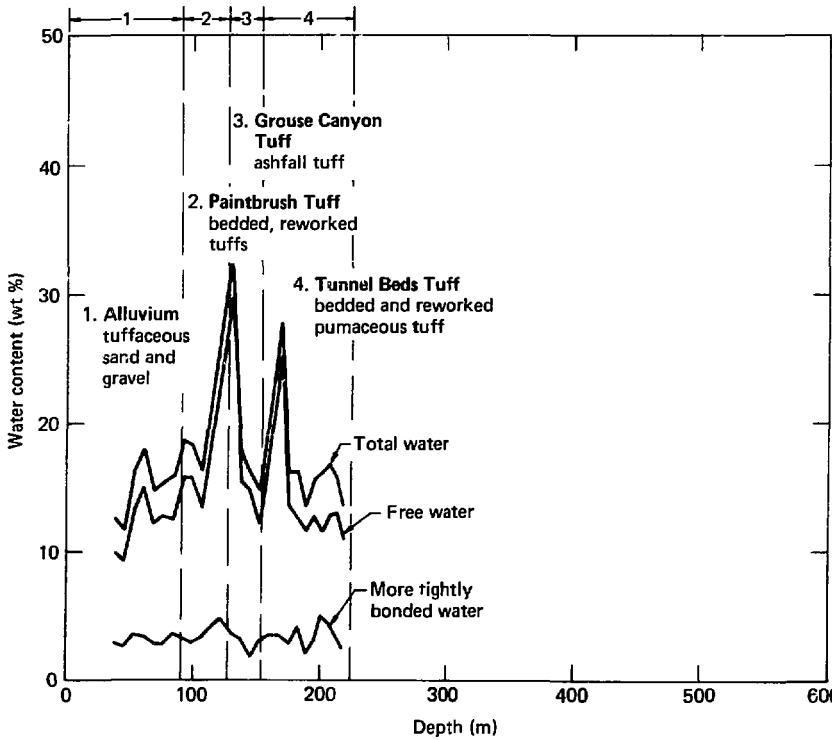

FIG. 13. Laboratory-eetermined water contents for U10bg, NTS.

CORRELATION OF TOTAL WATER CONTENT AND LITHOLOGY

Figures 2 through 13 also show lithological units for each hole. A lithologic log is prepared by an LLNL-Nevada field geologist from examination of samples and geophysical logs. An attempt to correlate total water content and known lithology proved interesting. It is possible to assign total water content values to lithologic units. Separation of alluvium and tuff by water content is possible. It is even possible to differentiate some of the tuffs by water content.

Distinguishing only alluvium and tuff lithologies yielded the following mean total water contents (weight fraction):

alluvium	0.14 ± .05
tuff	0.19 ± .04

Dividing the general category volcanic tuff into specific units gave these values of total water content (weight fraction):

Rainier Mesa	0.15 ± .01
Paintbrush	0.18 ± .03
Tunnel Beds	0.20 ± .04
Grouse Canyon	0.29 ± .02

Statistical tests were run in order to determine if the observed difference between the means of alluvium and tuff was significant and could be attributed to chance. The statistic t for two means tested the null hypothesis is $\mu_1 - \mu_2 = 0$ against the alternative $\mu_1 - \mu_2 \neq 0$, using Eq. (4). The null hypothesis states that the difference between the means is the same, and the samples cannot be distinguished. The samples were considered random, and of two normal populations with independent but not significantly different variables.

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad (4)$$

At a confidence level of .99, with $n_1 = 69$ and $n_2 = 291$, calculated t is 7.74, and t from the table is between 2.358 ($n = 120$) and 2.326 ($n = \infty$). Because the calculated t is larger, the null hypothesis is rejected; there is a significant difference between total water contents of alluvium and tuff.

An attempt was made to determine if statistical differences occurred between Grouse Canyon, Tunnel Beds, Paintbrush and Rainier Mesa tuffs. Table 2 shows the results of these tests.

At a .99 confidence level, it is apparent that there is a significant difference between total water contents of Grouse Canyon, Rainier Mesa, and Painthrush/Tunnel Beds tuffs. This difference does not exist for Paintbrush and Tunnel Beds tuffs, because these two tuffs are physically very similar.

At this point it may be informative to indicate that presently the individual values of water content reported for a drill hole are the laboratory values of free water only. Free water is the major contributor of total water content, and correlates well with it throughout the hole. It must be remembered, however, that these values are *less* than the actual total water content. It would probably be possible to assign free water content values to the various lithologies, using the above results. This report does not attempt to do this, being focused instead on future possibilities concerning the epithermal neutron log.

TABLE 2. Calculated and standard t values (.99 confidence level) for total water content of volcanic tuff units.

	Comparison lithology		
Test lithology	**Rainier Mesa**	**Paintbrush**	**Grouse Canyon**
Tunnel Beds	Calc. $t = 3.37$ $t_{36df} = 2.72$	Calc. $t = 0.32$ $t_{44df} = 2.70$	Calc. $t = 4.68$ $t_{33df} = 2.74$
Rainier Mesa		Calc. $t = 3.70$ $t_{20df} = 2.84$	Calc. $t = 13.97$ $t_{9df} = 3.25$
Paintbrush			Calc. $t = 5.56$ $t_{17df} = 2.90$

CONCLUSIONS

The laboratory procedure described in this report has been shown to determine the more tightly bonded water content with an error of ±0.59 wt%. This accuracy is acceptable for our work.

Total water content can be calculated for laboratory samples from free and more tightly bonded water contents. The largest amount of error possible in these values is equal to the error in the more tightly bonded water content.

It is possible to assign mean total water content values to the lithologic units at NTS. Where there is a significant statistical difference between these means, the possibility exists that the lithologic units are distinguishable by means of total water content determined for the sample. Thus, alluvium may be distinguished from tuff samples, and volcanic units may be divided into Grouse Canyon, Rainier Mesa, and Paintbrush/Tunnel Beds tuffs.

Once the epithermal neutron sonde is calibrated, it may be possible to recognize lithologic units from the determined water content values, according to the work described in this report. Water-content values would, of course, be used in association with information obtained from the gravimeter, magnetometer, downhole photography, and other useful logs.

ACKNOWLEDGMENTS

This project was organized by N. Howard to solve J. Hearst's need for total water content data. Most of the laboratory work was done as contract support to LLNL when I was a geology student at California State University, Hayward. W. Beiriger arranged the laboratory equipment. The lithologic logs for the drill holes were prepared by R. D. McArthur, J. D. Donithan, E. Ziegler, and A. C. Douglas of the LLNL-Nevada Geology Group. I would like to thank N. Burkhard for his guidance on the statistical aspects of the report, and N. Howard for her editorial comments.

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