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AN ALGORITHM FOR DETERMINING SOIL AND WATER HELIUM CONCENTRATIONS FROM HEADSPACE ANALYSES: EXAMPLES OF GEOCHEMICAL APPLICATIONS IN LONG VALLEY, CALIFORNIA AND THE FIJI ISLANDS

By

Kim R. Green

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Golden, Colorado

Date 5/2/84, 1984

Signed: Kim R. Green
Kim R. Green

Approved: Ronald W Klusman
Ron Klusman, Thesis Advisor

Golden, Colorado

Date 5/2/84, 1984

George H. Kennedy
George Kennedy, Head of Dept.

ABSTRACT

A helium survey based on the collection of soil samples was conducted in the Fiji Islands for the purpose of evaluating the petroleum potential of this area. Algorithms for calculating helium concentrations in soil and water samples from gaseous headspace analyses were found to be necessary and were developed. These algorithms were applied to data obtained from a second survey conducted in Long Valley, California. Similar anomaly patterns were observed between contour maps of uncorrected and algorithm-corrected helium concentrations in Long Valley, probably due to the uniformity of the soil samples. Corrected values do seem to show a reduction in survey noise.

Gaseous pore space and headspace volumes were found to have a large effect on the algorithm-corrected concentration of helium in gaseous pore space and must be accurately measured.

An evaluation of the Fiji data was done by estimating unmeasured parameters such as soil temperature, barometric pressure, pore space volume and headspace volume, and applying the algorithm for calculating helium in gaseous pore space concentrations. These types of estimations increased uncertaintly in the data. Differences between anomaly maps of uncorrected and algorithm-corrected helium concentrations may be due to variations in soil type. This would indicate a need for the use of algorithm-corrected concentrations for

correct survey interpretation.

Examination of helium emanations in Fiji suggests that there are anomalous areas on the eastern side of Viti Levu that may be associated with possible petroleum occurrences.

Algorithm-corrected helium concentrations may be needed in surveys where only a small number of samples can be collected; soil types vary; regional differences such as soil moisture and porosity occur; or helium emanations are of small magnitude. Corrections are also needed if comparisons are to be made between surveys conducted in different areas, or if a survey is repeated.

Recommendations for future surveys include the collection of larger amounts of soil, the selection of appropriate containers, allowance of proper equilibration times, avoidance of container overpressurizing, and determination of accurate soil pore space volumes and container pressures.

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INTRODUCTION

The tremendous expense of geophysical surveys and exploratory drilling has encouraged the development of geochemical surface prospecting techniques. In petroleum exploration, the gaseous element, helium, is being studied for its use as a geochemical indicator of oil and gas deposits.

Many of the petroleum reservoirs worldwide contain helium concentrations ranging from 100 ppm (by volume) to greater than 10% (Riley, 1980). Thus, subsurface entrapment of helium seems to parallel hydrocarbon accumulation. Within a petroleum reservoir, helium, being a mobile element, can slowly diffuse upwards through or around overlying cap rock and sediments to the surface. This can create an area of anomalous high helium concentrations in the near-surface environment. Migration and accumulation producing an apical type anomaly is schematically represented in figure 1. The detection of such anomalies during surficial helium surveys may then be indicative of petroleum deposits at depth.

A review of helium surveys carried out over a variety of known and suggested petroleum deposits is given by Roberts and others (1981). Results from eleven surveys conducted over known deposits indicated that for six of these areas, helium would have been of definite use in locating the deposits. Three more areas showed the presence of high helium anomalies, but precise correlation with the reservoir could not

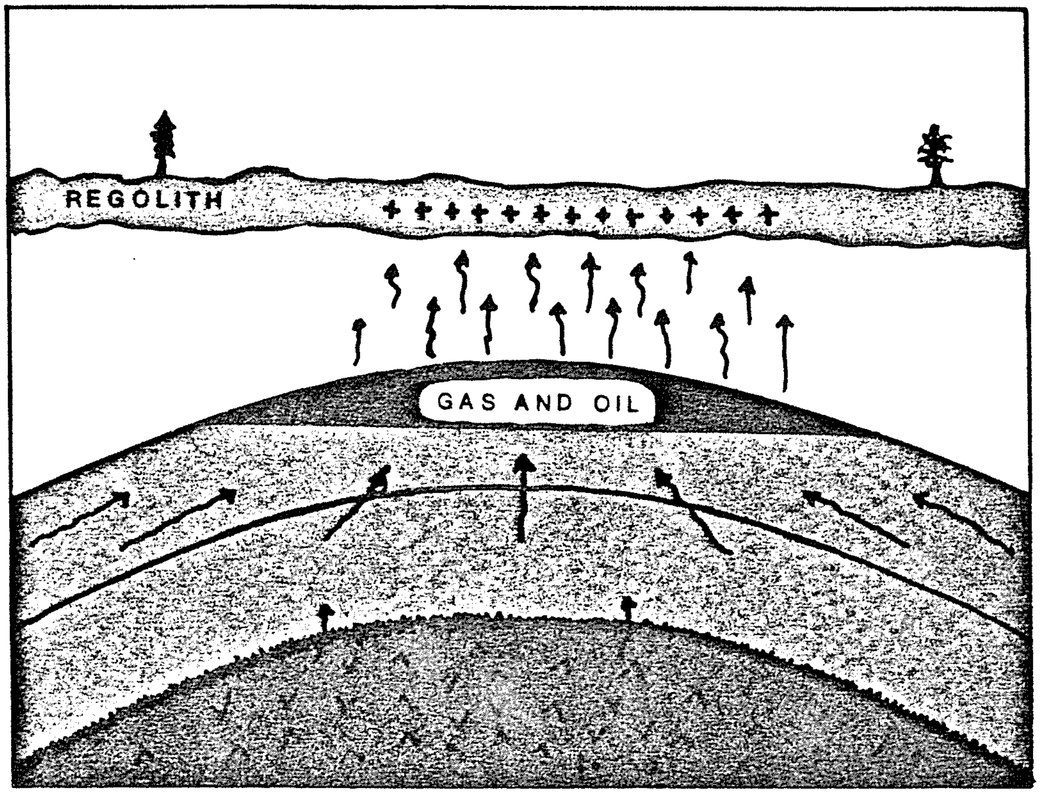

Figure 1. Apical type high helium anomaly produced in soils over a petroleum deposit.

be made. Two of the surveys did not show detectable helium anomalies.

The possibility exists that migrating helium could collect in a structural or stratigraphic trap where hydrocarbon concentrations are lacking. This could in turn produce helium anomalies unrelated to petroleum accumulations.

Research Objective

The initial objective of this research project was to evaluate the usefulness of helium surveys as part of a comprehensive petroleum exploration program conducted in the Fiji Islands, South Pacific. Petroleum occurrences are relaltively unstudied in this area, and Fiji has a different geologic setting and climate than that of previously conducted helium surveys.

Helium surveys can involve the collection of water, soil, or soil gas samples. For the Fiji helium survey, soil-gas sampling was planned, but soils were often found to have a high clay content and were frequently wet due to tropical weather conditions preventing the collection of such samples. Soil samples were therefore collected even though little research has been published on the use of soil samples in helium surveys. Analyses were accomplished by removing a gas sample from the air space or headspace at the top of the contained soil.

While conducting the Fiji survey, some soil-gas samples were also collected and analyzed. During the subsequent analysis of the collected data, the question arose as to whether the concentrations of helium measured in soil-gas could be directly compared to the concentrations of helium in headspace reported from the soil samples analyses. Examination of this question revealed that the concentrations of helium obtained from headspace analysis of the soil samples are not necessarily an accurate measure of the helium concentration that existed in the soil.

It was proposed, therefore, to derive algorithims for correcting helium concentrations measured from soils in the laboratory back to the original helium concentrations of soils in the field. At the same time, the use of soils in helium surveys could be examined. The collection of soil samples would greatly improve the utility of helium surveys since there are fewer climatic limitations imposed on sampling than with soil-gas collection.

The research objective therefore became:

1. Development of methods and techniques for using soil samples in helium surveys.
2. Development of algorithms to calculate the actual concentration of helium in a sample.
3. Examination of variables that affect the near-surface distribution of helium in soils.
4. Determination of how significant calculated concentrations are to the correct interpretation of a helium survey.
5. Possible reevaluation of the Fiji data, and the usefulness of helium as a petroleum exploration tool.

A second field study was conducted over the Long Valley caldera, near Mammoth Lakes California in order to facilitate the development of algorithms for determining actual concentrations of helium in soils, and the identification of associated parameters. This area has been undergoing unusual seismic activity and studies are being conducted by the U.S. Geological Survey to examine possible volcanic hazards. The helium survey presented here is part of this program. In this survey, measurements that were not taken in Fiji (such as soil temperatures, pressure, soil moisture and porosity) were made which allowed the calculation of helium concentrations in the soil samples. Thus, results from this study can be used to draw conclusions about the use of soils for helium surveys, identify variables that effect helium concentrations in soils, and determine the significance of the calculated, or corrected, helium concentration.

Geochemistry and Geologic Occurrences of Helium

Helium is present in minerals, rocks (sedimentary, crystalline and molten), natural gases, sea water, thermal springs, subsurface fluids, and the atmosphere. It occurs as a monatomic, gaseous molecule and has two stable isotopes, ^{3}He and ^{4}He.

It is probable that some primordial helium (^{3}He and ^{4}He) entrapped in the subsurface during degassing stages of the earth's formation still exists and is leaking to the atmosphere (Clarke, et al, 1969; Craig, et al., 1975). The origin of the majority of helium on earth, however, is the decay of radioactive elements.

Helium-4 is produced from the radioactive decay of uranium and thorium and their daughter products. These elements are found widely distributed throughout the earth. In the radioactive decay of ^{238}U to its final stable daughter, Pb-206, eight alpha particles are produced. These alpha particles, being positively charged, readily pick up free electrons to become inert, gaseous, ^{4}He atoms. This decay scheme is shown in figure 2. In addition to the uranium-238 series, ^{4}He can also be generated in the decay series of uranium-235 and thorium-232. The decay of these can be summarized as:

$$^{235}U \longrightarrow {}^{207}Pb + 7\ {}^{4}He$$

$$^{232}Th \longrightarrow {}^{208}Pb + 6\ {}^{4}He$$

(Moore and Esfandiari, 1971).

Uranium -238 and thorium -232 are the principal producers of ^{4}He, while nuclides rarer in abundance contribute only minor amounts.

The radiogenic decay of tritium generated in the crust (from ^{7}Li and ^{6}Li) and the atmosphere (from ^{14}N) represent an additional source of the ^{3}He isotope (Morrison and Pine, 1955). The production of ^{3}He is much lower than the production of ^{4}He. Its natural abundance is only 10^{-6} of the abundance ^{4}He (Mamyrin, et al., 1970). While the ratio of $^{3}He/^{4}He$ has been studied for use as an exploration technique for uranium deposits (Clarke and Kugler, 1973), a costly, high resolution mass spectrometer is needed to accurately measure this ratio. This limits its utility in exploration use. Unless otherwise noted, helium without an isotopic number will refer to ^{4}He in the remainder of this

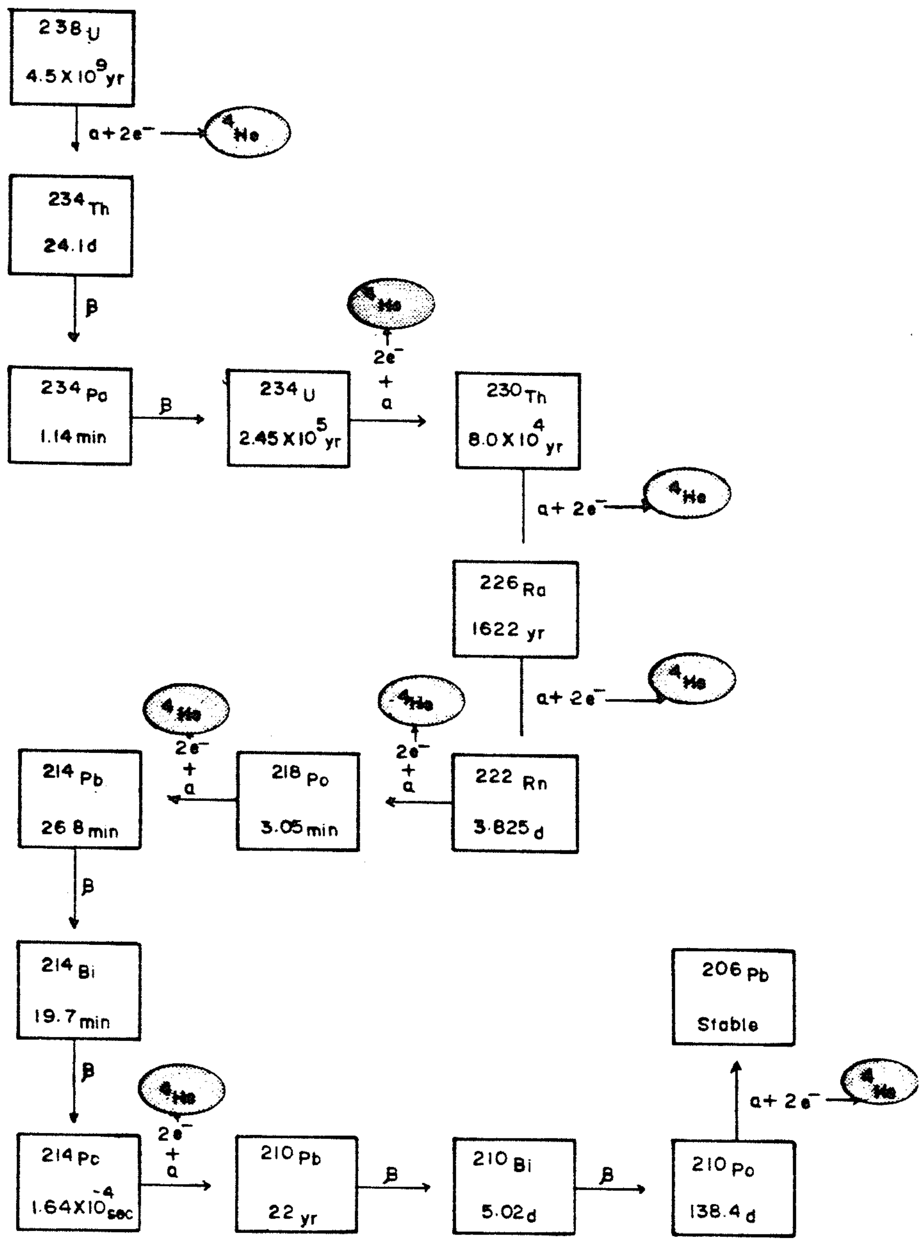

Figure 2. Decay scheme for ^{238}U, showing type of decay, decay products, half lives, and production of helium-4 (after Rose, Hawkes, and Webb, 1979).

report.

Helium has several properties associated with a good geochemical indicator. It is physically stable and being a noble gas it is chemically inert. It is also light (4 a.m.u.) and has a small atomic radius -- 0.93 Å (Huheey, 1968). Thus it is very diffusive. While the solubility of helium increases with pressure (i.e. depth) and temperature, it is only slightly soluble in water under surface conditions.

Helium is produced in the earth by radioactive decay at a rate of 1.125×10^{33} atoms per year (Reimer, 1976). Approximately half of the helium produced is formed in the crust, the remaining amount being produced in the mantle and core (Vinogradov, 1964). Atmospheric air is reported to contain 5.239 +/- 0.002 ppm He by volume (Glueckhauf, 1946). This value shows little variation despite environmental influences (Pogorski and Quirt, 1979). The concentration of helium in the subsurface exceeds that in the atmosphere. There is a continual flux through the crust to the atmosphere with eventual loss to space.

Once formed, helium will migrate upwards in the subsurface wherever channels of permeability are available. The mechanisms of migration are no doubt complex. Molecular diffusion accompanied by fluid transport seem to be the major mechanisms (Golubev, et al., 1974). The rate of transport in water is about six orders of magnitude higher than molecular diffusion, suggesting that migration is dominated by transport in the ground water system (Hurley, 1954). Thus, ground water may exercise considerable control over the distribution of He released into near-surface environment.

The rocks which generate helium have many differing degrees of helium retention (Martin, et al., 1977) and therefore, differing rates of release for migration to the surface. Therefore, the background levels of helium content can differ from one geologic environment to another.

As previously stated, uranium and thorium are widely distributed throughout the subsurface. Wherever they are present in deep igneous (basement) rocks, helium is generated and can migrate upwards. Uranium can be leached from igneous rocks by subsurface fluids and redeposited in all types of sediments and rocks. Redeposition of uranium in sedimentry rocks is commonly observed. These local occurrences would also produce helium that would then be available for upwards migration.

Helium found in oil and gas deposits is probably derived from several sources. Dissolved uranium may be concentrated from ground water into organic-rich strata typical of petroleum source rocks (Katz, 1969). These uraniferous shales and limestones, along with uranium and thorium scattered throughout the sedimentary section and basement rocks will produce He by radioactive decay which could migrate to and accumulate in structural or stratigraphic traps similarly to hydrocarbons. Uranium and thorium dissolved in circulating or migrating ground water or petroleum could become an alpha-emitting fluid, thus producing helium for migration to reservoirs (Moore, 1971).

Helium generation within a reservoir can occur if U and Th are dissolved in the petroleum (Moore, 1971). It is also possible that some uranium could be complexed out of a groundwater solution at the oil-water interface (Leventhal, 1982). Subsequent decay would produce additional He.

Variations in the abundance of helium in petroleum reservoirs would depend on several factors including the size of the reservoir, the concentration of radioactive minerals in the surrounding sedimentary rocks and basement rocks, the retention and leakage of helium in the reservoir, the rate of fluid flow through the structure, and the age of the source rocks. Older reservoir rocks (Paleozoic) contain larger amounts of helium (Tongish, 1980). This is probably a function of older rocks having had more time to generate helium than younger rocks.

The concentration level and areal extent of a petroleum related surficial helium anomaly depend on factors similar to those that determine helium's abundance in reservoirs. Major influences include permeability of the cap rock, depth of the deposit, and the concentrations of radioactive minerals producing helium in the subsurface.

Figure 1 illustrated the type of surficial anomaly that would be produced by the direct seepage of helium through the cap rock of a petroleum deposit followed by vertical migration to the surface (apical). A second type of anomaly pattern can occur as a halo of higher helium values at the surface partially or totally surrounding the underlying reservoir. The reasons for the occurrence of this type of anomaly are not well understood, but they may be the result of calcite infilling microfactures above a reservoir, thus blocking pathways for gas migration (Donovan, 1974). This cementation could be caused by the migration of hydrocarbons to the near-surface environment where they can be oxidized to bicarbonate or carbon dioxide, and precipitated out with calcium as calcium carbonate. This anomaly type is observed with a much smaller degree of frequency than apical ones.

In addition to petroleum reservoirs, there are other possible origins of helium anomalies in the near-surface. These are depicted in figure 3. Migrating groundwater can leach originally disseminaated uranium from an area and redeposit it as tabular or roll-front deposits. These deposits will then produce more helium than surrounding rock which can then migrate towards the surface producing detectable anomalies.

In a geothermal area, a magma body may expell or degas helium and other volatiles during cooling because of a drop in temperature or pressure. This excess helium can diffuse directly upwards, or mix with local ground water and be transported to the surface by convection and mass transport. The transport or flushing of helium is enhanced by higher temperatures of subsurface water such as are found in geothermal areas (Mazor, 1978/79). This helium can then enrich waters and soil gases producing anomalies.

Structures such as fractures or fault zones or even strong

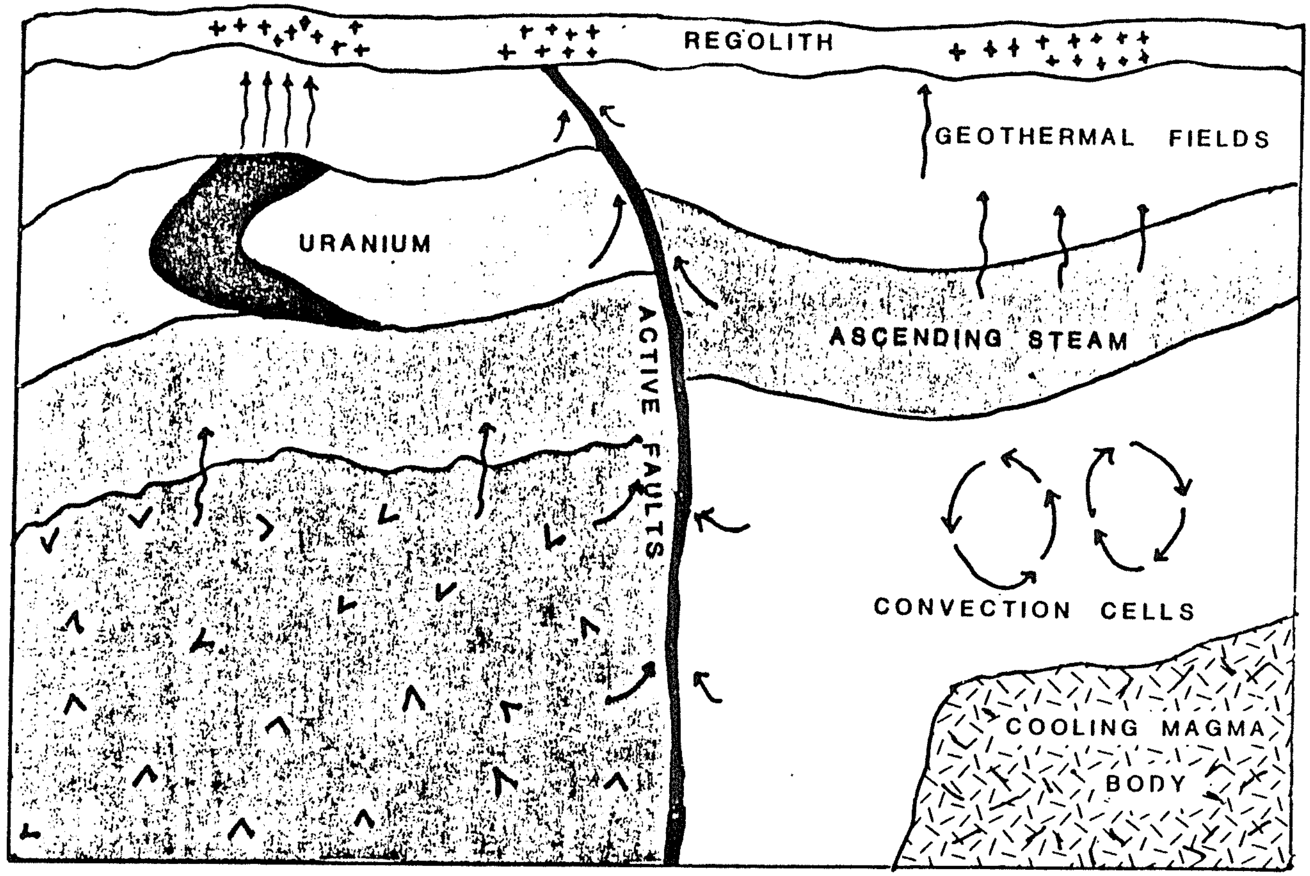

Figure 3. Possible origins for anomalously high helium concentrations in near-surface soils (after Clark, 1981).

jointing can collect helium in the subsurface along their length and act as channels for its flow to the surface. This can result in the observance of higher concentrations of helium above a fracture or fault zone than in surrounding areas. The migration and subsequent production of helium with regards to structural controls would depend on:

1. The degree of openness (effective permeability) of a fracture or fault zone.
2. The difference in permeability between a fracture or fault zone and the country rock.
3. The position of helium's source relative to the structure.
4. Geometrical-geological locations of the fault zone.

Geochemical gas studies have been done that link flucuations in near-surface helium concentrations to seismic events, or earthquakes. This is possibly due to preearthquake stress changes (Reimer, 1979).

Previous Work

Pierce and others (1964) studied the accumulation of helium in natural gases of the Texas Panhandle and relationships to uranium occurrences. Nikonov (1972) studied the accumulation of helium with varying types of petroleum reservoirs.

A review of helium emanometry as an exploration tool in the search for hydrocarbons is given by Pogorski and Quirt (1981). Results from tests over known petroliferous sites, conducted in cooperation with the

U.S. Geological Survey (Roberts, 1981) have been discussed earlier in this section.

Ball and Snowdon (1973) carried out helium in soil-gas surveys over areas of known oil and gas pools. Results demonstrated that helium may be used to distinguish between an oil and gas pool and a nearby dry structure.

Palacas and Roberts (1980) of the U.S. Geological Survey, report the detection of a small, positive anomaly (40-60 ppb above background) over the Sunniland oil field in South Florida, and a stronger anomaly (40-140 ppb) east of Immokalee. They suggest that these could represent helium leakage from subsurface oil accumulations, helium related to a possible buried uranium ore deposit, or helium generated by uraniferous phosphate deposits.

Holland and Emerson (1979) report finding a helium in soil gas anomaly in the east-central region of the Bush Dome reservoir, Cliffside field, Texas. This anomaly is displaced from the center of the field and top of the structure. They proposed that this displacement is caused by a strong ground water gradient in the area which flows southeastward in the Cliffside area.

Helium association with geothermal features has been examined by several researchers at the U.S. Geological Survey and elsewhere, including Hinkle (1978), Roberts and others (1975), Roberts (1975) and Mazor and Fournier (1973). It has been found that the helium concentration in soil-gases increase closer to a surface manifestation of geothermal activity such as hot springs. This suggests the possible utility of helium surveys in locating hidden geothermal reservoirs.

Much of the initial research involving helium as a geochemical tool has centered around its utilization in uranium exploration. Goldak (1973), Dyck (1976), and Clark et al. (1973, 1977) have conducted helium surveys in regions of uranium mineralization in Canada. Reimer (1976) and Friedman, Denton, and Roberts, of the U.S. Geological Survey, have also done extensive studies of helium's association with uranium and were instrumental in the practical development of a truck-mounted portable mass spectrometer for the field measurement of helium. Most studies have shown helium to be very useful in the exploration for uranium deposits.

Research has been conducted on the relationship of helium to structural features. High helium has been found in association with active fault zones by Reimer and Adkinson (1977) and in the current research area of Long Valley, California by Hinkle and Kilburn (1980). In the Soviet Union, Bulashevich and Bashorin (1973), and Plyusnin and others (1972) are using helium soil gas surveys to locate deep-seated faults. Eremeev and others (1972) have reported that helium can be useful in detecting mineralization along fault zones.

Many active faults periodically experience seismic tremors or earthquakes. Soil gas monitoring for helium may prove to be an important tool in predicting earthquakes. The tectonically active Matsushiro area of central Japan has experienced intense earthquake swarms. Wakita and others (1978) have observed that the helium concentrations over this area are higher than that of the surrounding areas. Reimer (1981) has also noted fluctuations in near-surface concentration of helium associated with earthquake activity. Currently research is centered on establishing trends of helium variation prior to seismic events.

Since anomalous concentrations of helium in the subsurface can be related to several geologic features, it is important that surveys are used in conjunction with geologic and geophysical studies to correctly establish anomalous features.

Much of the work using helium as a surficial geochemical indicator as described above has involved the collection of soil-gas samples. A soil-gas sample is collected by driving a hollow probe into the ground, inserting a hypodermic syringe into a rubber septum at the top of the probe, and withdrawing a small amount of interstitial soil gas at depth for analysis. A detailed description of these sampling and analyses techniques are given by Reimer and others (1979).

Hinkle (1980) of the U.S. Geological Survey and Pogorski and Pogorski (1982) of Chemical Projects, Ltd. have conducted helium surveys involving the collection of soil samples. Pogorski routinely makes corrections for determination of actual helium concentrations in such samples, but the algorithms are proprietary.

PART I

LONG VALLEY, CALIFORNIA

The Long Valley caldera is located along the eastern face of the Sierra Nevada mountains, 50 km northeast of the town of Bishop, California and 30 km south of Mono Lake (figure 4). The caldera is an eliptical depression encompassing approximately 450 square kilometers and was formed by the collapse of a magma chamber after a large volcanic eruption about 700,000 years ago (Bailey et al, 1976). This area contains a large active geothermal system. Surficial hydrothermal features such as hot springs and fumeroles are numerous and appear to be related to structural controls such as faults and fractures (Sorey et al., 1978). A detailed description of the geology of this area is given by Bailey et al.,1976.

Long Valley has been the location of unusual seismic activity since 1978. In addition to earthquakes and earthquake swarms with extension of existing fracturing and faulting, doming or uplift of the caldera floor has been observed. Additionally, the geothermal system within the caldera has been undergoing observable changes, such as the appearance of new steam vents.

The recent activity in this area has been linked to a proposed magma chamber that lies beneath the caldera at a depth of 6-8 km (Sorey et al.,1978, Bailey, 1982). It has been suggested that a tongue of magma may be moving towards the surface or that the magma chamber itself may be rising slightly and triggering the seismic activity. While the ultimate cause of this activity is not known, the U.S. Geological Survey is conducting geochemical and geophysical studies to

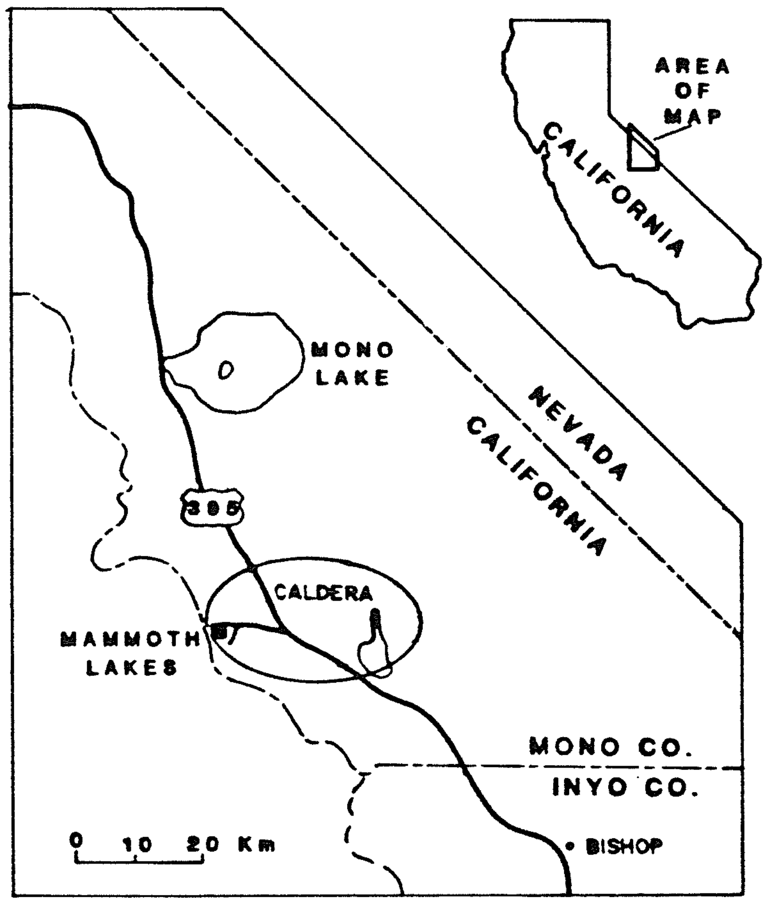

Figure 4. Location map of the Long Valley caldera (after Sorey et al., 1978).

detect significant changes and disturbances in the caldera system.

Helium's known association with many of the geologic features that are present in Long Valley suggests that it could be very useful in rapidly detecting and monitoring variations in gas mobility and distribution that might occur in the area. These variations could be used to infer changes in the Long Valley volcanic system.

The geochemical survey of helium in soils presented in this study was conducted in August, 1982, as part of the U.S. Geological Survey's investigations in Long Valley. As used here, this survey provided the opportunity to examine the usage of soil samples for helium surveys in a different geologic and climatic environment than Fiji. Algorithms were derived to calculate helium concentrations in soils and applied to data collected in Long Valley. From these results inferences were drawn as to how important the use of the algorithms are to the interpretation of a helium in soil survey. Additionally, parameters identified during the alogrithm derivation as affecting the calculated concentration of helium in soils were examined.

METHODS

The methods used to collect and analyze the Long Valley samples are reviewed below. Many of the techniques used in this survey were based upon an earlier helium in soils study conducted in Long Valley by Hinkle and Kilburn (1979). This study was performed to examine relationships between helium and geothermal features of the area. While not discussed here, these two surveys could be compared and used to assess possible changes in the volcanic system that have occurred in intervening years.

Sample Collection

In order to fully define the size and shape of anomaly patterns that the helium soil survey in Long Valley might yield. Two hundred and twelve soil samples were collected at approximately one kilometer intervals in a pattern resembling a grid. Soil sample locations approximate sites used by Hinkle and Kilburn in the 1978 survey and are shown in figure 5. Samples were taken by scraping away the top 15-20 cm of soil and placing soil from this depth into a 20-ml size Vacutainer brand blood specimen tube shown in figure 6. Vacutainers were filled to about three-quarters full, and the inclusion of small stones and organic debris was avoided. The tube was then capped with its rubber stopper and sealed with silicone sealent to help prevent leakage of gases.

Soil temperature and barometric pressure were measured. A soil thermometer was inserted next to the sample site to the depth of collection, allowed to equilibrate for about 3 minutes, and then read to the nearest 0.5^{o}C. Instantaneous pressure readings were taken to the nearest 0.1 inches (of Hg) using an anaeroid barometer.

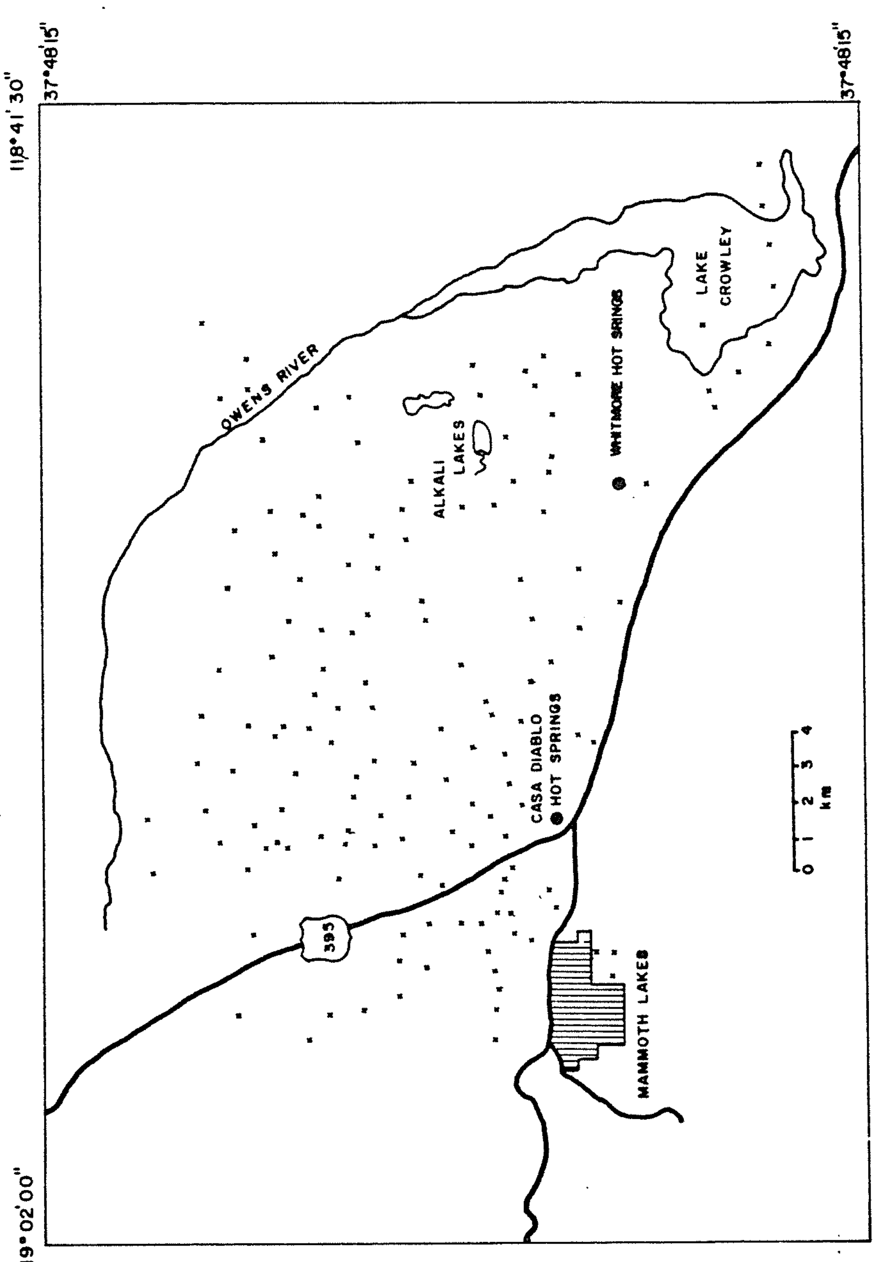

Figure 5. Sample location map for the Long Valley Survey.

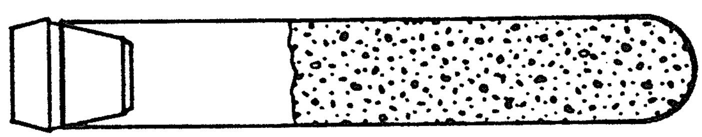

Figure 6. Vacutainer brand blood specimen tube used for soil sample collection.

Instrumentation

The laboratory spectrometer system used in this research was DuPont leak-detector mass spectrometer, that was tuned for a mass-to-charge ratio of 4 (He). This laboratory instrument was previously modified by the installation of a constant pressure inlet system which allows the introduction of gas samples from hypodermic syringes (Reimer, 1976).

All measurements of helium concentrations in soils, soil-gases, or water samples were made by filling a 10 cc hypodermic syringe with the gas sample and then injecting about 2.5 cc of the gas through a rubber septum into a evacuated gas reservoir, without any chemical separation. The injected gas causes the plunger of a glass syringe, vertically mounted on the reservoir, to rise. Constant pressure is maintained as the glass syringe falls by gravity. The gaseous sample then passes through a variable leak valve into the spectrometer. A liquid nitrogen chilled charcoal trap was used to freeze out possible interfering gases before ionization occurs. The instrument responses to helium and pressure are monitored by a strip chart recorder. A vacuum pump connected to the instrument allows the system to be evacuated after each sample analysis. This serves to flush the spectrometer of any remaining gas. A generalized diagram of the detection system is shown in figure 7. Further descriptions of the instrument are given by Reimer et al. (1979), and Roberts et al. (1975).

The spectrometer response is calibrated by interspersing standard

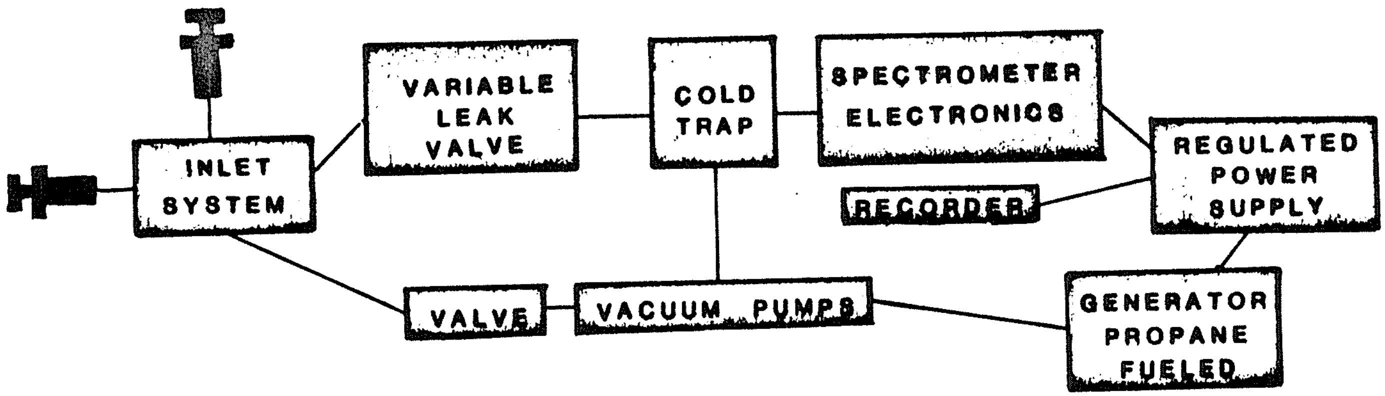

Figure 7. Generalized diagram of mass spectrometer used for helium detection (after Reimer, 1976).

air mixtures containing known concentrations of helium (reference gases). Each sample measurement was bracketed by the analysis of ambient (laboratory) air which contains 5240 ppb of He. Estimated precision is about +/- 10 ppb.

Soil Sample Analyses

Few studies have been done on determining the amount of time that collected soil samples should be allowed to equilibrate with headspace gas before analysis. A short study Hinkle and Kilburn (1979) using 20 ml Vacutainers to collect soils for helium analysis suggests that a two week equilibration period may be adequate. Thus, after collection, the Long Valley soil samples were left standing for two weeks to allow equilibration between helium in the soil and helium in the headspace of the Vacutainer to occur. The sealed samples were then placed in a 30^{o}C oven for a period of three days to allow equilibration at a known and constant temperature to occur.

At the time of analysis, the sample was removed from the oven and 5 cc of ambient air was added by injection with a hypodermic syringe. This was done to overpressurize the container allowing removal of a gaseous sample for analysis. The sample dilution this creates is corrected for in the data analysis. A vortex stirrer was then used to mix the added air with air inside the tube. The sample was vigorously stirred for 30 seconds. A two to three cc's gas sample was removed from the collection tube with a sryinge and immediately analyzed for helium content, using the DuPont mass spectrometer.

Concentrations of helium in headspace gas were reported as helium in air. These measurements reflect equilibration between helium in the soil sample, and helium of the gaseous headspace.

To allow the calculation of helium in soil concentrations, several other parameters were determined, including the amount of water, gaseous pore space, and gaseous headspace in each sample. The combined volumes of gaseous pore space and headspace within a sample container, referred to as the deadspace volume (Hinkle and Kilburn, 1979), was determined by inserting a needle attached to a hose and vacuum pump through the rubber septum of the Vacutainer and evacuating the sample for 30 seconds. After evacuation, a hypodermic syringe containing 20 cc of air was inserted into the sample container, and the amount of air drawn into the sample tube recorded as the deadspace volume, measured to the nearest 0.25 cc.

The height of the gaseous air space over a sample, or headspace, was measured to the nearest 1.0 mm. The volume of the headspace was geometrically calculated using the average diameter of 1.40 cm for a 20-ml Vacutainer. The volume of gaseous pore space in a sample was then found by subtracting the volume of headspace from the volume of deadspace.

A determination of the amount of water in samples was done by accurately weighing each sample and then drying in a 70^{o}C oven until a constant weight was obtained. The difference was taken to be the weight of water in the sample. Using the weight of water in a sample, the volume of water was calculated by assuming a density of 1.0g/cc.

The pressure inside the sealed Vacutainer, or container pressure, was not actually measured, but calculated using the changes in thermodynamic conditions from the field to laboratory:

$$\frac{T_l P_f}{T_f} = P_c$$

where

T_l = temperature of the sample prior to analysis (lab)

P_f = barometric pressure at time of sample collection (field)

T_f = temperature of soil at time of collection (field)

P_c = pressure inside container at time of analysis (lab)

This is a valid estimation of the pressure inside the container if there is no gas produced or consumed within the tube or lost due to leakage in either direction.

CALCULATION OF HELIUM CONCENTRATIONS

It has been stated that concentrations of helium obtained from headspace analysis of soil samples are not necessarily an accurate measure of the helium concentration that existed in the soil.

This can be illustrated by examining the effect of atmospheric dilution in a contained sample. Figure 8 shows an example of two collected soil samples. Helium concentraations in soils are generally

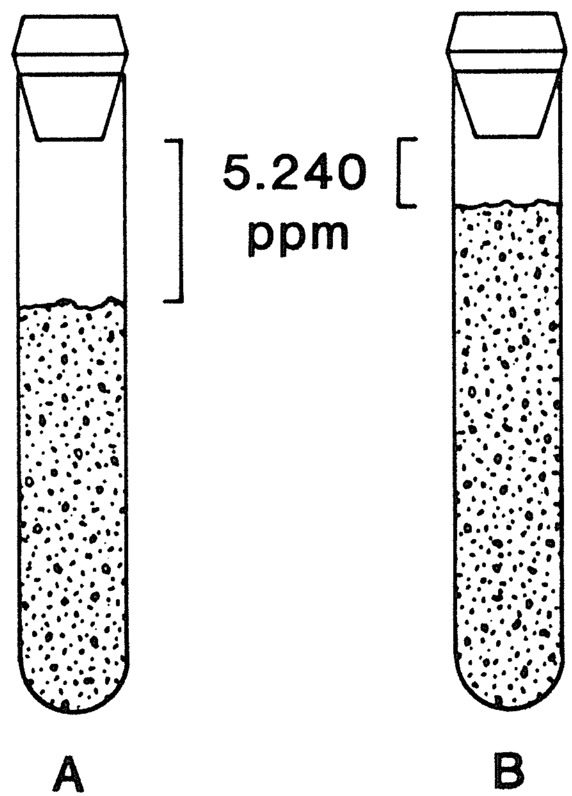

Figure 8. Contained soil samples, illustrating the effect of atmospheric dilution.

found to be equal to or greater than that of atmospheric helium (illustrated as 5.240 ppm). Soils A and B may actually have the same helium concentrations, but since less of sample A was collected, it experiences a greater amount of dilution by the atmospheric helium (5.240 ppm) enclosed with it than B.

Therefore, although the actual concentrations may be equal, helium in headspace analyses will show a different concentration for each sample, and sample B would appear to have a higher concentration of helium than sample A. Therefore, a great deal of caution should be used when interpreting the results of helium in headspace analyses from soil samples. It would be of greater value to correct helium in headspace back to the original helium concentrations of the soil samples.

To determine the actual concentration of helium in a sample, an equation can be derived that takes raw data obtained from the analysis of an extracted gas sample--headspace analysis--and generates the concentration of helium that existed in a sample at the time of collection. This concentration of helium can be determined in different ways depending on which part of the sample is considered to contain most of the helium. If there is more measurable gaseous porespace in a sample than soil moisture, the helium concentration can be given as volumes of helium per volumesof porespace. If a sample contains more soil moisture (or is totally composed of water) the helium concentrations can be expressed as volumes of helium per volumes of water. The overall effect of the following calculations is to return the laboratory conditions of analysis to the field conditions at the time of sample collection.

<u>Helium in Soils</u>

In a soil sample, helium is present in several forms. The helium that significantly contributes to the measured concentration in a soil sample is derived from helium that is a component of interstitial gas in soil pores, and helium in solution in soil moisture.

In the following derivation, it was found that by measuring gaseous pore space and headspace volumes and the amount of soil moisture in a sample, the original helium content can be calculated based on thermodynamic differences between field and laboratory conditions. Note that the measured helium in headspace value (by mass spectrometric analysis) is not necessarily the total helium present in a sample, but the concentration of helium in the headspace of a container that is in equilibrium with the sample.

The helium present in a sample container at the time of collection should equal the amount of helium in the container at the time of analysis, assuming that no gas leakage has occured:

$$He_{initial} = He_{final} \qquad (1)$$

The helium initially present in a sample can be said to consist of helium present in the soil moisture, helium present in the gaseous soil pores, and helium present in the gas above a sample upon filling and sealing of the container:

$$He_{Initial} = I_p + I_w + I_h \qquad (2)$$

where

I_p = moles of helium initially present in gaseous soil pores (or pore space)

I_w = moles of helium initially present in soil moisture

I_h = moles of helium initially present in the headspace of sample container

Helium present in a sealed sample at the time of analysis consists of helium present in soil moisture, helium in the gaseous soil pores and helium present in gas above the sample:

$$He_{final} = F_p + F_w + F_h \qquad (3)$$

where

F_p = moles He present at time of analysis in soil pores

F_w = moles He present in water or soil moisture at time of analysis

F_h = moles He present in headspace at time of analysis

Substituting equation (2) and (3) into equation (1) yields:

$$I_p + I_w + I_h = F_p + F_w + F_h \qquad (4)$$

The amount of helium originally present in the soil would be represented by $I_p + I_w$. Rearranging to separate these terms out yields:

$$I_p + I_w = F_p + F_w + F_h - I_h \qquad (5)$$

Thus, if expressions for the terms on the right side of equation (5) can be found, the amount of helium originally present in the soil ($I_p + I_w$), and consequently the concentration of helium in a soil sample can be determined.

It is a very good approximation to consider helium an ideal gas. Thus, many thermodynamic relations can be directly applied in the following calculations.

To evaluate the change in state of an ideal or perfect gas, Boyle's and Charles' laws can be combined and applied:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{(constant number of moles, ideal gas)} \qquad (6)$$

This relation can be used to correct measured volumes of gas to volumes that would exist at standard conditions (STP), of 1 atm pressure, and 273.16°K.

The following sections describe the derivation of expressions for terms appearing in equation (5).

Calculation of I_h. The moles of helium present in the headspace at the time of analysis can be determined if the volume of helium in the headspace is known. If this volume is corrected to standard conditions, it can be multiplied by the gram-molecular volume of a gas:

$$I_h = V_{hc} \times 1\text{mole}/22.4\ \text{l}$$

or

$$I_h = V_{hc} \times 1\text{mole}/22414\text{cc} \qquad (7)$$

where

V_{hc} = volume of helium in headspace at time of collection corrected to STP (in cc's)

At the time of collection, the concentration of helium collected in the headspace of a sample container would equal the concentration of helium in the atmosphere, since no time has elapsed for equilibration between helium in the soil and helium in the headspace to occur.

As previously stated, the concentration of helium in the atmosphere is found to be relatively constant at to 5.240 ppm by volume. The parts per million concentration term can then be expressed as volumes of helium per volumes of air or:

$$\text{He ppm} = \frac{\text{cc He}}{10^6 \text{cc air}} = \frac{5.240 \text{ cc He}}{10^6 \text{cc air}} \qquad (8)$$

Therefore, the initial volume of helium present in the headspace of the sample container can be found by:

$$\frac{5.240 \text{ cc He}}{10^6 \text{cc air}} \cdot V_h = V_{hf} \qquad (9)$$

where

V_h = volume of headspace in sample container, in cc air

V_{hf} = volume of helium in headspace at time of collection (field), in cc He.

Using equation (6), the volume of helium in the headspace, V_{hf}, can be corrected to STP:

$$\frac{P_f V_{hf}}{T_f} = \frac{1\text{atm } V_{hc}}{273.16^{\circ}\text{K}} \qquad (10)$$

where

P_f = absolute pressure in field at time of collection, in atmospheres

T_f = temperature of soil at time of collection, in $^{\circ}$K

V_{hc} = volume of helium in headspace at time of collection, corrected to STP, in cc's He

Rearranging (10):

$$V_{hc} = \frac{V_{hf}\ P_f\ 273.16^{o}K}{T_f \cdot 1atm} \qquad (11)$$

Substituting (9) into (11):

$$V_{hc} = \frac{\left(\frac{5.240cc\ \ He}{10^6 cc\ air} \cdot V_h\right) \cdot \ P_f\ 273.16^{o}K}{T_f \cdot 1atm} \qquad (12)$$

Substitution of (12) into (7) gives I_h, the desired expression for the moles of helium present in the headspace at the time of analysis:

$$I_h = \frac{\left(\frac{5.240\ cc\ He}{10^6 cc\ air} \cdot V_h\right) P_f\ 273.16^{o}K}{T_f \cdot 1atm} \cdot \frac{1\ mole}{22414\ cc} \qquad (13)$$

This term can be later substituted into equation (5) for the determination of the amount of helium originally present in a soil sample.

Calculation of F_h. Reported concentrations of helium measured spectrometrically represent the total concentration-in ppm by volume - of helium measured in the gas above a soil at the time of analysis, This can be represented as a volume fraction:

$$He\ ppm = \frac{[Y]\ cc\ He}{10^6\ cc\ air} \qquad (14)$$

where Y is the number of cc's of helium in 10^6cc's air.

The volume of helium present in the headspace at the time of analysis can then be found in a similar way to I_h--the initial volume of helium present in the headspace (equation (9)):

$$\frac{[Y] \text{ cc He}}{10^6 \text{cc air}} \cdot V_h = V_{hl} \qquad (15)$$

V_h = volume of headspace in sample container (in cc)

V_{hl} = volume of helium (in cc) present in headspace at time of analysis (lab)

This can be corrected to the volume that would exist under standard conditions:

$$\frac{P_c \; V_{hl}}{T_l} = \frac{1\text{atm } V_{fc}}{273.16^{o}\text{K}} \qquad (16)$$

where

V_{fc} = volume of helium in headspace at time of analysis (final), corrected to STP (in cc's)

T_l = temperature of sample at time of analyis (lab, in ^{o}K)

P_c = pressure in sample container at time of analysis (in atm)

Since the sample container is sealed, its pressure is not that of the lab, but the pressure inside the container. This differs from the pressure it was collected at (field), mainly due to changes in temperature.

Rearranging (15):

$$V_{fc} = \frac{V_{hl} \cdot P_c \cdot 273.16^{o}\text{K}}{T_l \cdot 1\text{atm}} \qquad (17)$$

Substituting (14) into (16):

$$V_{fc} = \frac{\left(\frac{[Y]\ cc\ He}{10^6 cc\ air} \cdot V_h\right) P_c\ 273.16^oK}{T_1 \cdot 1atm} \qquad (18)$$

Following equation (7), the volume of helium present in the headspace at the time of analysis, V_{fc}, can be converted to moles of helium present in the headspace at the time of analysis, F_h, by:

$$F_h = V_{fc} \cdot \frac{1\ mole}{22414cc} \qquad (19)$$

Substituting (18) into (19) gives the final form of F_h--the moles of helium in the headspace at the time of analysis:

$$F_h = \frac{\left(\frac{[Y]\ cc\ He}{10^6 cc\ air} \cdot V_h\right) \cdot P_c \cdot 273.16^oK \cdot 1\ mol}{T_1 \cdot 1atm \qquad 22414cc} \qquad (20)$$

This term will also be substituted into equation (5).

<u>Calculation of F_p.</u> The moles of helium present in the gaseous soil pore space at the time of analysis can be determined in a manner similar to the previous calculations.

The concentration of helium measured in the headspace at time of analysis should be equivalent to the concentration of helium in the gas pore space at the time of analysis (assuming complete equilibration). Therefore, the volume of helium present in the pore spaces (gaseous) can be found by:

$$\frac{[Y]cc\ He}{10^6 cc\ air} \cdot V_p = V_{p1} \qquad (21)$$

where

V_p = volume of gaseous pore space in soil (in cc)

V_{pl} = volume of helium in the gaseous pore space at time of analysis (lab, in cc)

This is corrected to standard conditions:

$$\frac{P_c V_{pl}}{T_l} = \frac{1atm \;\; V_{pc}}{273.16^{o}K} \qquad (22)$$

where

V_{pc} = volume of helium in gaseous pore space at time of analysis, corrected to STP (in cc's)

Rearranging (22):

$$V_{pc} = \frac{V_{pl}\ P_c\ 273.16^{o}K}{T_l \cdot 1atm} \qquad (23)$$

Substituting (21) into (23)

$$V_{pc} = \frac{\left(\frac{[Y]cc\ He}{10^6 cc\ air} \cdot V_p\right) \cdot P_c \cdot 273.16^{o}K}{T_l \cdot 1atm} \qquad (24)$$

V_{pc}, the volume of helium in the gas pore space at the time of analysis, can be converted to the desired term, F_p--the moles of helium present in the gaseous soil pore space at the time of analysis by:

$$F_p = V_{pc} \cdot \frac{1\ mole}{22414\ cc} \qquad (25)$$

Substituting (24) in (25) yields the final form of F_p:

$$F_p = \frac{\frac{[Y]cc\ He}{10^6 cc\ air} \cdot V_p \cdot P_c \cdot 273.16^{o}K}{T_l \cdot 1atm} \cdot \frac{1\ mole}{22414cc} \qquad (26)$$

This represents another term to be substituted into equation (5)--the moles of helium in the gaseous pore space at the time of analysis.

Calculation of F_w. The moles of helium dissolved in the soil moisture of a sample at the time of analysis can be examined using Henry's law, which states that the mass of a sparingly soluble gas (i) that dissolves in a definite volume of liquid at a given temperature is directly proportional to the equilbrium partial vapor pressure of that gas:

$$P_i = X_i K_i \text{ ideally dilute solution} \quad (27)$$

where:

P_i = partial pressure of gas i above a liquid

X_i = the mole fraction of dissolved gas i present in the liquid at a given temperature

K_i = the Henry's law constant for gas i in a liquid at a given temperature and pressure

The solubility of helium in water is 4.5 x 10^{-8}cc He/g H_2O at 35^oC and latm pressure of air (Weiss, 1971). Thus the concentration of helium in water is low enough for the solution to be considered to follow ideal behavior, and Henry's law holds well. Therefore, the amount of helium dissolved in the soil moisture (assuming pure water) at the time of analysis can be calculated as follows:

$$P_{He} = X_{He} \, {}^{1}K_{He} \quad (28)$$

where

X_{He} = the mole fraction of dissolved helium in soil moisture at the specified (lab) temperature

P_{He} = partial pressure of helium in the sample container above the soil sample

$^{1}K_{He}$ = the Henry's law constant in moles H_2O atm He per moles He at temperature of analysis (lab) and standard pressure

An expression for the partial pressure of helium in the sample container above a soil can be derived. The partial pressure, P_i, of a gas in a gas mixture (ideal or nonideal) is defined as:

$$P_i = X_i \, P \quad \text{(any gas mixture)} \qquad (29)$$

where

X_i = the mole fraction of i in the mixture

P = the total pressure of the mixture

Therefore,

$$P_{He} = {}^{g}X_{He} \cdot P_c \qquad (30)$$

where

P_{He} = partial pressure of helium in the gas mixture (air) above soil in the container

${}^{g}X_{He}$ = mole fraction of helium in the gas mixture (air) within the container

Again, P_c is the pressure (total) inside the container at the time of analysis.

A mole fraction is defined as:

$$X_i = \frac{n_i}{n_{tot}} \qquad (31)$$

where the total moles of all species present is n_{tot} and n_i is the moles of component i present. For the situation under consideration, this can be represented as:

$$X_{He} = \frac{n_{He}}{(n_{air} + n_{He})} \qquad (32)$$

where n_{air} represents the moles of gaseous components in air.

Since the concentration of helium in air is in the parts per million range, the moles of He, n_{He}, is much smaller than the moles of air, n_{air}:

$$n_{He} << n_{air} \qquad (33)$$

Therefore n_{tot} can be assumed to be the number of moles of air only, and the mole fraction of helium present in the gas mixture (air) within a sample container can be considered to be:

$$^{g}X_{He} = \frac{n_{He} \text{ in air}}{n_{air}} \qquad (34)$$

Instead of the mole fraction, $^{g}X_{He}$, a volume fraction can be used by observing the following relationships:

$$n_{He} = \frac{P_c\ V_{He}}{RT_1}, \quad \text{and} \quad n_{air} = \frac{P_c V_{air}}{RT_1} \qquad (35)$$

(using the ideal gas law and assuming ideal gas behavior)

where

V_{He} = the number of cc's of He in the gas of a container

V_{air} = the number of cc's of air in a container

R = the ideal gas constant

By substitution of equations (35) into (34), the mole fraction, $^{g}X_{He}$, then becomes:

$$ {}^{g}X_{He} = \frac{n_{He}}{n_{air}} = \frac{\dfrac{P_c V_{He}}{RT_1}}{\dfrac{P_c\ V_{air}}{RT_1}} \qquad (36) $$

Cancellation of equivalent terms in (36) yields:

$$ {}^{g}X_{He} = \frac{n_{He}}{n_{air}} = \frac{V_{He}}{V_{air}} \qquad (37) $$

The volume fraction that appears in (37) is equivalent to the concentration term (ppm) that is used in helium analyses:

$$ \frac{V_{He}}{V_{air}} = \frac{[Y]\text{cc He}}{10^6\text{cc air}} \qquad (38) $$

Substituting (38) into (37) yields a new expression for the mole fraction, ${}^{g}X_{He}$:

$$ {}^{g}X_{He} = \frac{[Y]\text{ cc He}}{10^6\text{cc air}} \qquad (39) $$

Substituting this expression for the mole fraction into equation (30) then becomes:

$$ P_{He} = \frac{[Y]\text{ cc He}}{10^6\text{cc air}} \cdot P_c \qquad (40) $$

This gives the expression for the partial pressure of helium in the gas mixture above the soil, and can be used in equation (28) (Henry's Law).

Since the amount of helium present in the water is the quantity of ultimate interest, we return to equation (28) and rearrange:

$$X_{He} = \frac{P_{He}}{{}^{1}K_{He}} \qquad (41)$$

Substituting equation (40) into (41):

$$X_{He} = \frac{\frac{[Y]cc\ He}{10^{6}cc\ air} \cdot P_c}{{}^{1}K_{He}} \qquad (42)$$

An expression for X_{He}, has now been obtained. This relates directly to the desired quantity--the amount of helium present in the water at the time of analysis:

$$X_{He} = \frac{n_{He}\ in\ H_2O}{n_{tot}} \qquad (43)$$

where:

X_{He} = the mole fraction of He present in the sample moisture

n_{He} = the moles of He dissolved in the water at the time of analysis

n_{tot} = the moles of dissolved He plus the moles of water

As previously stated, the solubility of atmospheric helium in water is very low, ($<10^{-7}$ $ccHe/ccH_2O$), therefore, the moles of helium present in the water of a sample is very small relative to the number of moles of H_2O:

$$n_{He} \ll n_{H_2O} \qquad (44)$$

Thus in equation (43) n_{tot} is approximated by:

$$X_{He} = \frac{n_{He}}{n_{H_2O}} \qquad (45)$$

where

n_{H_2O} = moles of soil moisture (water) present in soil

Substitution of equation (45) into (42) and rearrangement yields:

$$n_{He} = \frac{\frac{[Y]\text{cc He}}{10^6\text{cc air}} \cdot P_c}{{}^1K_{He}} \cdot n_{H_2O} \qquad (46)$$

The number of moles of helium present in the water at the time of analysis has been previously labeled as the quantity under consideration, F_w. Therefore:

$$n_{He} = F_w \qquad (47)$$

Substituting (47) into (46):

$$F_w = \frac{\frac{[Y]\text{cc He}}{10^6\text{cc air}} \cdot P_c}{{}^1K_{He}} \cdot n_{H_2O} \qquad (48)$$

If the assumption is made that the water in the soils is fresh, its density would equal 1.0 g/cc. Multiplying this value by the volume of water (cc's) in the soil would yield the grams of water in a sample. Division of the mass of water by the gram molecular weight of water allows the moles of water present in the soil to be calculated:

$$n_{H_2O} = \frac{(1.0\ g/cc \cdot V_w)}{18.01\ g/mol} \qquad (49)$$

where

V_w = volume of water (moisture) present in soil sample (in cc)

Substitution of (49) into (48) yields the final form of F_w, the moles of He dissolved in the soil moisture, or water, of a sample at the time of analysis:

$$F_w = \frac{\frac{[Y]cc\ He}{10^6 cc\ air} \cdot P_c}{{}^1K_{He}} \cdot \frac{(1.0g/cc \cdot V_w)}{18.01\ g/mol} \qquad (50)$$

Equation (50) represents the final term to be used in equation (5) for the determination of the amount of helium originally present in a soil sample.

Calculation of $I_p + I_w$. Reexamining equation (5):

$$I_p + I_w = F_p + F_w + F_h + I_h \qquad (5)$$

it can be seen that expressions for each term on the right hand side of the above equation have now been determined. Substitution of these expressions, (13), (20), (26) and (50) into (5) yields an equation for calculating the total amount of helium originally present in a soil sample, both in the gaseous pore space and moisture, under the field conditions:

$$I_p + I_w = \left[\frac{\left(\frac{[Y]\text{cc He}}{10^6\text{cc air}} \cdot V_p\right) \cdot P_c \cdot 273.16^{\circ}\text{K}}{T_1 \cdot 1\text{atm}} \cdot \frac{1\text{ mole}}{22414\text{cc}} \right]$$

$$+ \left[\frac{\frac{[Y]\text{cc He}}{10^6\text{cc air}} \cdot P_c}{{}^{1}K_{He}} \cdot \frac{(1.0\text{ g/cc} \cdot V_w)}{18.01\text{ g/mol}} \right]$$

$$+ \left[\frac{\left(\frac{[Y]\text{cc He}}{10^6\text{cc air}} \cdot V_h\right) \cdot P_c\ 273.16^{\circ}\text{K}}{T_1 \cdot 1\text{atm}} \cdot \frac{1\text{ mol}}{22414\text{cc}} \right]$$

$$- \left[\frac{\frac{5.240\text{ cc He}}{10^6\text{cc air}} \cdot V_h \cdot P_f \cdot 273.16^{\circ}\text{K}}{T_f \cdot 1\text{atm}} \cdot \frac{1\text{ mol}}{22414\text{ cc}} \right] \quad (51)$$

Equation (51) can be somewhat simplified. Combining the terms for F_h, F_p, and I_h and rearranging yields:

$$I_p + I_w = \frac{273.16^{\circ}\text{K} \cdot \frac{1\text{ mole}}{22414\text{ cc}}}{1\text{atm}} \left[\frac{\frac{[Y]\text{ cc He} \cdot P_c}{10^6\text{cc air}}}{T_1} (V_h + V_p) - \frac{\frac{5.240\text{ cc He}}{10^6\text{cc air}} \cdot V_h \cdot P_f}{T_f} \right]$$

$$+ \left[\frac{\frac{[Y]\text{cc He}}{10^6\text{cc air}} \cdot P_c}{{}^{1}K_{He}} \cdot \frac{(1.0\text{ g/cc} \cdot V_w)}{18.01\text{ g/mol}} \right] \quad (52)$$

Again, the sum of these terms gives the total amount of helium, in moles, initially present in the moisture and gas pore space of a soil sample.

Partitioning of Helium between I_p and I_w. Assuming the total amount of helium in a soil's gaseous pore space and soil moisture are originally (at the time of collection) in equilbrium, a mass balance type relationship can be established to determine how the total amount of helium initially present is partitioned between the two.

An expression can be written involving the moles of helium in a gaseous mixture using the ideal gas law, which relates pressure, temperature and moles of a gas:

$$PV = nRT \qquad (53)$$

For helium present in gaseous pore space, this becomes:

$$P_{He}\, V_p = n_p R T_f \qquad (54)$$

where

P_{He} = partial pressure of helium in the gaseous moisture of the pore space (atm)

n_p = moles of helium present in pore space at time of analysis

R = ideal gas constant--0.0821 l atm per (mole ^{o}K) or 82.05 cc atm per (mole ^{o}K)

V_p = volume of gaseous pore space in cc's (as previously defined)

T_f = temperature in field at time of collection in ^{o}K (as previously defined)

The partial pressure instead of total pressure--can be used in the above relation since only the moles of helium in the volume of porespace is being examined.

As previously stated by equation (2) the moles of helium initially present in the gaseous soil porespaces is symbolized as:

$$n_p = I_p \qquad (55)$$

Substitution of (55) into (54) yields:

$$P_{He} V_p = I_p RT_f \qquad (56)$$

To now examine the amount of helium initially disssolved in the soil moisture we return to Henry's law:

$$P_{He} = X_{He} \, {}^{f}K_{He} \qquad (57)$$

where

P_{He} = the partial pressure of helium in the gaseous phase, at field conditions (atm)

X_{He} = the mole fraction of helium dissolved in the soil moisture at the specified (field) temperature

${}^{f}K_{He}$ = the Henry's law constant for field temperature and latm

The units of the Henry's law constant are the same as previously used in equation (28)-- moles H_2O atm He per moles of He.

Following equation (45), X_{He} can be written as:

$$X_{He} = \frac{n_w}{n_{H_2O}} \qquad (58)$$

where

n_w = moles of helium originally present in soil moisture

n_{H_2O} = the moles of water present in soil

Substitution of (58) into (57) yields:

$$P_{He} = \frac{n_w \, {}^{f}K_{He}}{n_{H_2O}} \qquad (59)$$

As previously defined by equation (2) the moles of helium initially present in the soil moisture is symbolized as:

$$n_w = I_w \qquad (60)$$

Substituting (60) into (59):

$$P_{He} = \frac{I_w}{n_{H_2O}} \cdot {}^{f}K_{He} \qquad (61)$$

and substitution of the expression for the moles of water present, n_{H_2O}, from equation (49) yields:

$$P_{He} = \frac{I_w}{\dfrac{1.0 g/cc \cdot V_w}{18.01 g/mol}} \cdot {}^{f}K_{He} \qquad (62)$$

Noting that both equation (56) and (62) contain the variable for the partial pressure of helium originally in the gaseous phase allows the initial amount of helium in the water and gaseous pore space to be related. Rearranging (56):

$$P_{He} = \frac{I_p RT_f}{V_p} \qquad (63)$$

Setting (63) equal to (62) yields:

$$\frac{I_p \; RT_f}{V_p} = \frac{I_w}{\dfrac{1.0 g/cc \cdot V_w}{18.01 g/mol}} \cdot {}^{f}K_{He} \qquad (64)$$

The moles of water (initial), I_w, can now be solved for in terms of I_p. For simplification in rearrangements the following symbolism is made:

$$I_p + I_w = S \quad (65)$$

Where S is the total number of moles of helium initially present in a soil sample.

Substituting (65) into equation (5):

$$S = F_p + F_w + F_h - I_h \quad (66)$$

S would then be equal to the terms on the right side of equation (52).

Rearranging (65):

$$I_w = S - I_p \quad (67)$$

Substitutiton of the above expression for I_w, (67), into (64) yields:

$$\frac{I_p RT_f}{V_p} = \frac{(S-I_p)}{\frac{1.0g/cc \cdot V_w}{18.01\,g/mol}} \cdot {}^fK_{He} \quad (68)$$

With the completion of the above step, an equation is obtained that can be solved for the variable I_p--the moles of helium initially present in the soil pore spaces--in terms of known or measured quantities. Solving for I_p can be done in a series of steps:

$$\frac{I_p \cdot RT_f}{V_p} = \frac{{}^fK_{He} \cdot S}{\frac{1.0g/cc \cdot V_w}{18.01\,g/mol}} - \frac{{}^fK_{He}\; I_p}{\frac{1.0g/cc\; V_w}{18.01\,g/mol}} \quad (69)$$

$$\frac{I_p \cdot R \cdot T_f}{V_p} + \frac{{}^fK_{He}\; I_p}{\frac{1.0g/cc \cdot V_w}{18.01\,g/mol}} = \frac{{}^fK_{He} \cdot S}{\frac{1.0g/cc \cdot V_w}{18.01\,g/mol}} \quad (70)$$

$$I_p \cdot \left(\frac{R \cdot T_f}{V_p} + \frac{f_{K_{He}}}{\frac{1.0 g/cc \cdot V_w}{18.01 g/mol}} \right) = \frac{f_{K_{He}} \cdot S}{\frac{1.0 g/cc\ V_w}{18.01 g/mol}} \tag{71}$$

$$I_p = \frac{\dfrac{f_{K_{He}} \cdot S}{\frac{1.0 g/cc \cdot V_w}{18.01\ g/mol}}}{\dfrac{f_{K_{He}}}{\frac{V_w \cdot 1.0 g/cc}{18.01 g/mol}} + \dfrac{RT_f}{V_p}} \tag{72}$$

Rearranging (72), the expression for determining the moles of helium initially present in the pore space of a soil sample, I_p, becomes:

$$I_p = \frac{\dfrac{f_{K_{He}} \cdot 18.01\ g/mol}{V_w \cdot 1.0 g/cc} \cdot S}{\dfrac{f_{K_{He}} \cdot 18.01 g/mol}{V_w \cdot 1.0 g/cc} + \dfrac{RT_f}{V_p}} \tag{73}$$

The expression for the term S, defined to be $I_p + I_w$, can now be substituted into equation (73). The term S would equal the right side of equation (52). This yields the final form of an equation for determining the moles of helium originally present in the gaseous soil pore space:

$$I_p = \frac{{}^{f}K_{He} \cdot 18.01\,g/mol}{V_w \cdot 1.0g/cc} \cdot \left[\frac{273.16^oK \dfrac{1\ mol}{22414cc}}{1\ atm} \cdot \left[\frac{\dfrac{[Y]\ cc\ He}{10^6 cc\ air} \cdot P_c}{T_1} (V_h + V_p) - \frac{\dfrac{5.240\ cc\ He}{10^6 cc\ air} \cdot V_h \cdot P_f}{T_f} \right] \right.$$

$$\left. + \left[\frac{\dfrac{[Y]\ cc\ He}{10^6 cc\ air} \cdot P_c}{{}^{1}K_{He}} \cdot \frac{(1.0g/cc \cdot V_w)}{18.01\,g/mol} \right] \right]$$

$$/ \left[\frac{{}^{f}K_{He} \cdot 18.01\ g/mol}{V_w \cdot 1.0g/cc} + \frac{RT_f}{V_p} \right] \qquad (74)$$

Having determined an expression for the moles of helium initially in the gaseous soil pore space, an equation can now be derived for the moles of helium initially dissolved in the soil moisutre. Returning to the mass balance relationship as established in equation (67) and rearranging yields:

$$I_w = S - I_p$$

Substitution of I_p from equation (73) gives:

$$I_w = S - \left(\frac{\dfrac{{}^{f}K_{He} \cdot 18.01\,g/mol}{V_w \cdot 1.0g/cc} \cdot S}{\dfrac{{}^{f}K_{He} \cdot 18.01\,g/mol}{V_w \cdot 1.0g/cc} + \dfrac{RT_f}{V_p}} \right) \qquad (75)$$

Rearranging (75):

$$I_w = S \cdot \left(1 - \frac{\dfrac{{}^{f}K_{He} \cdot 18.01\,g/mol}{V_w \cdot 1.0\,g/cc}}{\dfrac{{}^{f}K_{He} \cdot 18.01\,g/mol}{V_w \cdot 1.0\,g/cc} + \dfrac{RT_f}{V_p}} \right) \quad (76)$$

Again, the term S would equal the right side of equation (52) . Substituting this expression into (76), yields an equation for determining the moles of helium originally present in the soil moisture:

$$I_w = \left[\frac{273.16^{o}K \cdot \dfrac{1\ mole}{22414\ cc}}{1\ atm} \left[\frac{\dfrac{[Y]\ cc\ He \cdot P_c}{10^6 cc\ air}}{T_1} \cdot (V_h + V_p) - \frac{\dfrac{5.240\ cc\ He}{10^6 cc\ air} \cdot V_h \cdot P_f}{T_f} \right] + \left[\frac{\dfrac{[Y] cc\ He \cdot P_c}{10^6 cc\ air}}{{}^{1}K_{He}} \cdot \frac{(1.0g/cc \cdot V_w)}{18.01\,g/mol} \right] \right]$$

$$\cdot \left[1 - \frac{\dfrac{{}^{f}K_{He} \cdot 18.01\,g/mol}{V_w \cdot 1.0\ g/cc}}{\dfrac{{}^{f}K_{He} \cdot 18.01\,g/mol}{V_w \cdot 1.0g/cc} + \dfrac{RT_f}{V_p}} \right] \qquad (77)$$

Calculation of Initial Concentrations of Helium in Gaseous Soil Pore Space. Expressions for the concentration of helium (instead of moles) in a soil sample are now desired. Again, this can be expressed in different ways, depending on which part of the sample is considered to have most of the excess helium.

If there is a significant amount of gaseous pore space in a soil sample, the helium concentration can be calculated as volumes of helium per volumes of gaseous porespace. If the sample is very wet or totally composed of water, the helium concentration may be given as volumes of helium per volumes of water in soil.

The calculated values, whether as gaseous volumes or wet volumes in a soil sample, will yield equivalent results since the helium in water is in equilibrium with the helium in porespace. When applicable, it may be more desirable to report helium concentrations as volumes of helium per volumes of gaseous porespace.

A feasible representation of volumes of helium per volumes of gaseous porespace would be:

$$\frac{\text{cc He}}{\text{cc pore space}} \qquad (78)$$

Under standard conditions this would equal:

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{{}^{p}V_{He}}{{}^{STP}V_{p}} \qquad (79)$$

where

${}^{p}V_{He}$ = volume of helium, in cc's initially present in gaseous soil pore space calculated at STP

${}^{STP}V_{p}$ = volume of gaseous pore space, in cc's, in a soil sample that would exist under standard conditions

The development of expressions for the terms on the right side of equation (79) yields the desired concentration of helium in gaseous pore space of a soil sample.

The moles of helium, I_p, present in the gaseous pore spaces of the sample initially are calculated by equation (74). Under standard conditions, the volume of helium in the pore space can be found by multiplying by the inverse of the gram-molecular volume of a gas (as discussed in (7)).

$$I_p \cdot \frac{22414\text{cc}}{1\text{ mol}} = {}^{p}V_{He} \qquad (80)$$

Using the measured volume of pore space, V_p, and the field temperature and pressure, the volume of pore space that would exist under standard conditions, ${}^{STP}V_{p}$, can be calculated by using Boyles and Charles laws:

$$\frac{V_p\ P_f}{T_f} = \frac{{}^{STP}V_{p} \cdot 1\text{atm}}{273.16^{\circ}\text{K}} \qquad (81)$$

Solving equation (81) for ${}^{STP}V_p$:

$$^{STP}V_p = \frac{V_p P_f \cdot 273.16^oK}{T_f \cdot 1atm} \qquad (82)$$

Substituting (82) into (79) yields:

$$\frac{cc\ He}{cc\ pore\ space} = \frac{{}^{p}V_{He}}{\dfrac{V_p P_f \cdot 273.16^oK}{T_f \cdot 1atm}} \qquad (83)$$

Rearranging:

$$\frac{cc\ He}{cc\ pore\ space} = \frac{{}^{p}V_{He} \cdot T_f \cdot 1atm}{V_p P_f \cdot 273.16^oK} \qquad (84)$$

Substituting in the expression for ${}^{p}V_{He}$ from equation (80) yields:

$$\frac{cc\ He}{cc\ pore\ space} = \frac{I_p \cdot \dfrac{22414cc}{1\ mol} \cdot T_f \cdot 1atm}{V_p \cdot P_f \cdot 273.16^oK} \qquad (85)$$

Substituting in I_p (from equation 74)) into equation (85):

$$\frac{\text{cc He}}{\text{cc pore space}} =$$

$$\Bigg\{ \Bigg[\frac{{}^{f}K_{He} \cdot 18.01\,\text{g/mol}}{V_w \cdot 1.0\,\text{g/cc}} \cdot \left[\frac{273.16^{o}K \quad \dfrac{1 \text{ mole}}{22414 \text{ cc}}}{1 \text{ atm}} \right] \cdot$$

$$\left[\frac{\dfrac{[Y]\text{cc He}}{10^{6}\text{cc air}} \cdot P_c}{T_1} (V_h + V_p) - \frac{\dfrac{5.240 \text{ cc He}}{10^{6}\text{cc air}} \cdot V_h \cdot P_f}{T_f} \right]$$

$$+ \left[\frac{\dfrac{[Y]\text{cc He}}{10^{6}\text{cc air}} \cdot Pc}{{}^{1}K_{He}} \cdot \frac{(1.0\,\text{g/cc} \cdot V_w)}{18.01\,\text{g/mol}} \right] \Bigg] \Bigg]$$

$$/ \left[\frac{{}^{f}K_{He} \cdot 18.01\,\text{g/mol}}{V_w \cdot 1.0\,\text{g/cc}} + \frac{RT_f}{V_p} \right] \Bigg\}$$

$$\cdot \left(\frac{T_f \; 22414\text{cc} \cdot 1\text{atm}}{V_p \cdot P_f \; 1 \text{ mol} \cdot 273.16^{o}K} \right) \qquad (86)$$

Equation (86) can be simplified using several steps. Rearranging yields:

$$
\begin{aligned}
\frac{\text{cc He}}{\text{cc pore space}} = {} & \frac{T_f}{V_p P_f} \cdot \frac{22414\text{cc}}{1\text{ mol}} \cdot \frac{1\text{ atm}}{273.16^{o}\text{K}} \left\{ \left[\frac{{}^{f}K_{He} \cdot 18.01\text{g/mol}}{V_w \cdot 1.0\text{g/cc}} \cdot \right. \right. \\
& \left[\frac{273.16^{o}\text{K} \quad \dfrac{1\text{ mol}}{22414\text{cc}}}{1\text{ atm}} \cdot \left[\frac{\dfrac{[Y]\text{ He cc}}{10^{6}\text{cc air}} \cdot P_c}{T_1} \right. (V_h + V_p) \right. \\
& \left. - \frac{\dfrac{5.240\text{ cc He}}{10^{6}\text{cc air}} \cdot V_h \cdot P_f}{T_f} \right] \\
& \left. + \left[\frac{\dfrac{[Y]\text{ccHe} \cdot P_c}{10^{6}\text{cc air}}}{{}^{1}K_{He}} \cdot \frac{(1.0\text{g/cc} \cdot V_w)}{18.01\text{g/mol}} \right] \right] \Bigg] \\
& \left. \cdot \left[\frac{1}{\dfrac{{}^{f}K_{He} \cdot 18.01\text{g/mol}}{V_w \cdot 1.0\text{ g/cc}} + \dfrac{RT_f}{V_p}} \right] \right\} \qquad (87)
\end{aligned}
$$

Rearranging equation (87):

$$\frac{\text{cc He}}{\text{cc pore space}} =$$

$$\frac{Tf}{V_p P_f} \cdot \frac{22414\text{cc} \cdot 1\text{atm}}{1\text{ mol } 273.16^{o}K} \left\{ \left[\frac{273.16^{o}K \cdot \frac{1\text{ mol}}{22414\text{cc}}}{1\text{ atm}} \right. \right.$$

$$\cdot \left[\frac{\frac{[Y]\text{ cc He}}{10^6\text{cc air}} \cdot P_c}{T_1} \cdot (V_h+V_p) \right.$$

$$\left. - \frac{\frac{5.240\text{ cc He}}{10^6\text{cc air}} \cdot V_h \cdot P_f}{T_f} \right] + \left[\frac{\frac{[Y]\text{cc He}}{10^6\text{cc air}} \cdot P_c}{{}^{I}K_{He}} \cdot \frac{(1.0\text{g/cc} \cdot V_w)}{18.01\text{ g/mol}} \right] \Bigg]$$

$$\left. \cdot \left[\frac{{}^{f}K_{He} \cdot 18.01\text{ g/mol}}{V_w \cdot 1.0\text{ g/cc}} \cdot \left[\frac{1}{\frac{{}^{f}K_{he} \cdot 18.01\text{ g/mol}}{V_w \cdot 1.0\text{ g/cc}} + \frac{RT_f}{V_p}} \right] \right] \right\} \quad (88)$$

Rearranging (88):

$$\frac{\text{cc He}}{\text{cc pore space}} =$$

$$\frac{T_f}{V_p P_f} \left\{ \frac{22414\ \text{cc} \cdot \text{latm}}{1\ \text{mol}\ 273.16^{\circ}\text{K}} \left[\left[\frac{273.16^{\circ}\text{K} \cdot 1\ \text{mol}}{\text{latm}\ 22414\ \text{cc}} \cdot \left[\frac{\frac{[Y]\text{cc He}}{10^6\ \text{cc air}} \cdot P_c}{T_1} \cdot (V_h + V_p) \right. \right. \right. \right.$$

$$\left. - \frac{\frac{5.240\ \text{cc He}}{10^6\ \text{cc air}} \cdot V_h \cdot P_f}{T_f} \right] + \left[\frac{\frac{[Y]\ \text{cc He}}{10^6\ \text{cc air}} \cdot P_c}{{}^{1}K_{He}} \cdot \frac{(1.0\ \text{g/cc} \cdot V_w)}{18.01\ \text{g/mol}} \right] \Bigg]$$

$$\left. \cdot \left[\frac{\frac{{}^{f}K_{He} \cdot 18.01\ \text{g/mol}}{V_w \cdot 1.0\ \text{g/cc}}}{\frac{{}^{f}K_{He} \cdot 18.01\ \text{g/mol}}{V_w \cdot 1.0\ \text{g/cc}} + \frac{RT_f}{V_p}} \right] \Bigg] \right\} \qquad (89)$$

Multiplication and cancellation of equivalent terms yield:

$$\frac{\text{cc He}}{\text{cc pore space}} =$$

$$\frac{T_f}{V_p P_f} \left\{ \left[\left[\frac{\frac{[Y]\ \text{cc He} \cdot P_c}{10^6 \text{cc air}}}{T_1} (V_h + V_p) - \frac{\frac{5.240\ \text{cc He}}{10^6 \text{cc air}} \cdot V_h \cdot P_f}{T_f} \right] \right. \right.$$

$$\left. + \left[\frac{\frac{[Y]\ \text{cc He} \cdot P_c}{10^6 \text{cc air}}}{{}^{1}K_{He}} \cdot \frac{1.0 \text{g/cc} \cdot V_w}{18.01 \text{g/mol}} \cdot \frac{22414 \text{cc} \cdot 1 \text{atm}}{1 \text{ mol } 273.16^{\circ}\text{K}} \right] \right]$$

$$\left. \cdot \frac{\frac{{}^{f}K_{He} \cdot 18.01 \text{g/mol}}{V_w \cdot 1.0 \text{ g/cc}}}{\frac{{}^{f}K_{He}\ 18.01 \text{g/mol}}{V_w \cdot 1.0 \text{g/cc}} + \frac{RT_f}{V_p}} \right\} \qquad (90)$$

and finally further cancellation and rearrangement yields:

$$\frac{\text{cc He}}{\text{cc pore space}} =$$

$$\frac{T_f}{V_p P_f} \cdot \frac{1}{1 + \dfrac{R T_f \, V_w \cdot 1.0 \text{ g/cc}}{V_p \, {}^{f}K_{He} \cdot 18.01 \text{ g/mol}}} \left[\left[\frac{\dfrac{[Y] \text{cc He}}{10^6 \text{cc air}} \cdot P_c}{T_1} \cdot (V_h + V_p) \right. \right.$$

$$\left. - \frac{\dfrac{5.240 \text{ cc He}}{10^6 \text{cc air}} \cdot V_h \cdot P_f}{T_f} \right]$$

$$\left. + \left[\frac{\dfrac{[Y] \text{ cc He}}{10^6 \text{cc air}} \cdot P_c}{{}^{1}K_{He}} \cdot \frac{1.0 \text{ g/cc } V_w}{18.01 \text{ g/mol}} \cdot \frac{22414\text{cc} \cdot 1\text{atm}}{1 \text{ mol } 273.16^{\circ}\text{K}} \right] \right] \qquad (91)$$

The headspace concentration of helium in a sample can be expressed as the measured quantity--ppm He, absolute. For reference, table 1 summarizes definitions of terms used in the derivation. For general and computer use, terms used in equation (91) kept solely to show consistency of units may be dropped:

Table 1. Summary of Terms Used in Final Equations.

${}^{f}K_{He}$	=	Henry's Law constant, at temperature (°C) of sample during collection, in moles H_2O atm He per moles He, at standard pressures (1 atm). Available as moles of H_2O mm Hg per moles of He from graph in Appendix A.
V_w	=	Volume of water or soil moisture in sample (in cc's).
ppm He	=	Reported value for helium concentration in headspace of sample, absolute
T_l	=	Temperature of sample (laboratory) at time of analysis (in °K)
P_c	=	Pressure inside sample container at time of analysis (in atm)
V_h	=	Volume, (in cc) of headspace in sample container
V_p	=	Volume in (cc) of pore space in soil sample
P_f	=	Pressure of surficial sample at time of collection (in atm) Taken to be atmospheric pressure
T_f	=	Temperature of soil at time of collection (°K)
${}^{l}K_{He}$	=	Henry's law constant at temperature (°C) of sample at time of analysis, units of moles H_2O atm He per moles He and standard pressure (1 atm). Available as moles of H_2O mm Hg per moles He from graph in Appendix A
R	=	Ideal gas law constant or 82.05 cc atm per mol °K

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{T_f}{V_p P_f} \cdot \frac{1}{1 + \dfrac{R T_f V_w}{V_p \, {}^{f}K_{He} \cdot 18.01}}$$

$$\left[\left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{T_l} \cdot (V_h + V_p) - \frac{5.24 \cdot 10^{-6} \cdot V_h \cdot P_f}{T_f} \right]\right.$$

$$\left. + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c \cdot V_w \cdot 22414}{{}^{l}K_{He} \cdot 18.01 \cdot 273.16} \right]\right] \qquad (92)$$

A drafted version of the equation (expanded) for calculating the concentration of helium in the gaseous pore space of a soil sample appears in figure 9.

$$\frac{\text{cc He}}{\text{cc psp}} = \frac{Tf}{Vp\ Pf} \times \frac{1}{1 + \dfrac{RVw\ Tf}{Vp\ {}^{f}K_H \times 18.01\ \text{g/mol}}} \times \left[\frac{\dfrac{\text{ppm He}}{10^6}\ Pc\ Vh}{T_l} \right.$$

$$+ \frac{\dfrac{\text{ppm He}}{10^6}\ Pc\ Vp}{T_l} - \frac{\dfrac{5.240\ \text{ccHe}}{10^6\text{cc air}}\ Vh\ Pf}{Tf} +$$

$$\left. \frac{\dfrac{\text{ppm He}}{10^6}\ Pc\ Vw \times 22.414\ \text{l/mol} \times 1000}{273.16°\text{K} \times 18.01\ \text{g/mol} \times {}^{l}K_H} \right]$$

Figure 9. Dervived equation (expanded from equation (91)) for the calculation of helium concentrations in the gaseous pore space of a soil.

Since measured concentrations of helium in headspace are often reported as ppm helium in excess of air, the concentration of helium in air (5.240 ppm) must be added to the reported concentration to give the absolute helium concentration measured:

$$\text{ppm [He] reported} + 5.240 \text{ ppm} = \text{ppm [He] abs.}$$

The expression cc He/cc porespace x 10^{+6} also represents ppm helium in the gaseous porespace of a soil sample, or (abbreviated) ppm He in psp.

Temperatures are often measured in degrees Celsius, rather than degrees Kelvin. A correction can be made to allow direct use of ^{o}C in equation (92):

$$\text{ppm He} \times 10^{-6} = \frac{\text{cc He}}{\text{cc pore space}} =$$

$$\frac{({}^{c}T_f + 273.16)}{V_p P_f} \cdot \frac{1}{1 + \dfrac{R\,({}^{c}T_f + 273.16) \cdot V_w}{V_p \; {}^{f}K_{He}}}$$

$$\cdot \left[\left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{({}^{c}T_1 + 273.16)} (V_h + V_p) - \frac{5.24 \cdot 10^{-6} \cdot V_h \cdot P_f}{({}^{c}T_f + 273.16)} \right] \right.$$

$$\left. + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c \cdot V_w \cdot 22414}{{}^{1}K_{He} \cdot 18.01 \cdot 273.16} \right] \right] \quad (93)$$

where

$^{c}T_{f}$ = Temperature of soil at time of collection in ^{o}C

$^{c}T_{l}$ = Temperature of sample at time of analysis in ^{o}C

If pressures are measured in millimeters Hg instead of atmospheres, a conversion can be made by dividing the measured pressure by 760 mm/atm. If the Henry's law constants used, as in Appendix A, are in the units of moles of H_2O (mm Hg) per mole of He, they must also be converted to reflect atmospheres of pressure by the division of 760 mm/atm.

With the above considerations, equation (93) represents the derived equation for calculating the concentration (absolute ppm) of helium in the gaseous pore space of a soil sample from measured values of helium in the headspace above the soil.

Helium in Wet Soils

For a very wet soil sample which still has some gaseous porespace, but in which most of the helium is contained in the water, it may be desirable to report the original helium concentration as the amount of helium present in the soil moisture, rather than the amount of helium in the gaseous pore space. An equation to calculate this value can be derived similarly to the helium in pore space derivation. In a very wet-soil sample, the helium measured in the headspace over the sample mainly reflects the exsolution of helium dissolved in the soil moisture.

Calculation of the Initial Concentration of Helium in Wet Soil Samples. While cc's of He in cc's of water is not strictly a concentration term, as previously stated, the concentration of helium in a water sample can be expressed as volume of helium per volume of moisture in a sample.

The equivalent volume of helium initially present in the soil moisture (at STP) can be found from the initial number of moles of helium dissolved in the water, I_w, using terms defined in the previous section. Multiplying by the inverse of the gram molecular volume of gas yields:

$$I_w \cdot \frac{22414\text{cc}}{1\text{ moles}} = {}^{p}V_{He} \quad (94)$$

where

${}^{p}V_{He}$ = equivalent volume (in cc) of helium initially present in the water of a sample of STP

Unlike a volume of a gas, the volume of soil moisture in a sample does not need to be corrected to STP conditions. Pressure differences between standard pressure and typical field pressures would have a negligible effect on the volume of soil moisture, due to the incompressibility of a liquid. Temperature differences between standard temperature (0^{o}C) and an extreme soil temperature of 30^{o}C would result in a change in the volume of water of less than 0.5%. This degree of error is small enough (compared to others in the corrections) that the effect of temperature changes on the volume of soil moisture may also be ignored. Therefore, dividing ${}^{p}V_{He}$ by the measured volume of water or soil moisture, V_w, gives the desired term--the volume of helium in the volume of soil moisture:

$$\frac{{}^{p}V_{He}}{V_w} = \frac{cc\ He}{cc\ H_2O} \qquad (95)$$

Substituting (94) into (95):

$$\frac{cc\ He}{cc\ H_2O} = \frac{I_w \cdot \dfrac{22414\ cc}{1\ mol}}{V_w} \qquad (96)$$

Substituting in the expression for I_w from equation (77) into (96) yields:

$$\frac{cc\ He}{cc\ H_2O} =$$

$$\left\{ \left[\frac{273.16^oK \quad \frac{1\ mol}{22414\ cc}}{1\ atm} \cdot \left[\frac{\frac{[Y]\ cc\ He}{10^6 cc\ air} \cdot P_c}{T_1} \right. \cdot (V_h + V_p) \right. \right.$$

$$\left. - \frac{\frac{5.240\ cc\ He}{10^6 cc\ air} \cdot V_h \cdot P_f}{T_f} \right]$$

$$\left. + \left[\frac{\frac{[Y]\ cc\ He}{10^6 cc\ air} \cdot P_c}{{}^1K_{He}} \cdot \frac{(1.0g/cc \cdot V_w)}{18.01\ g/mol} \right] \right]$$

$$\left. \cdot \left[1 - \frac{\frac{{}^fK_{He} \cdot 18.01\ g/mol}{V_w \cdot 1.0\ g/cc}}{\frac{{}^fK_{He} \cdot 18.01 g/mol}{V_w \cdot 1.0g/mol} + \frac{RT_f}{V_p}} \right] \right\}$$

$$\cdot \frac{22414cc}{1\ mole \cdot V_w} \qquad (97)$$

Simplifying (97) yields:

$$\frac{cc\ He}{cc\ H_2O} =$$

$$\left\{\left[\frac{273.16^{o}K \cdot \frac{1\ mol}{22414cc}}{1\ atm}\left[\frac{\frac{[Y]cc\ He}{10^6 cc\ air} \cdot P_c}{T_l}(V_h+V_p) - \frac{\frac{5.240\ cc\ He}{10^6 cc\ air} \cdot V_h \cdot P_f}{T_f}\right] + \left[\frac{\frac{[Y]cc\ He}{10^6 cc\ air} \cdot P_c}{{}^{l}K_{He}} \cdot \frac{1.0 g/cc \cdot V_w}{18.01 g/mol}\right]\right]\right.$$

$$\left. \cdot \left[1 - \frac{1}{1 + \frac{RT_f V_w \cdot 1.0 g/mol}{V_p \cdot {}^{f}K_{He} \cdot 18.01 g/mol}}\right]\right\} \cdot \frac{22414cc}{1\ mol \cdot V_w} \qquad (98)$$

For general and computer use, terms in equation (98) used to show consistency of units may be dropped and the headspace concentration of helium in a sample can be expressed as the measured quantity (ppm He $\cdot$ 10^{-6}):

$$\frac{cc\ He}{cc\ H_2O} = \left\{ \left[\frac{273.16}{22414} \left[\frac{ppm\ He \cdot 10^{-6} \cdot P_c}{T_1} \cdot (V_h+V_p) - \frac{5.24 \cdot 10^{-6} \cdot V_h \cdot P_f}{T_f} \right] + \left[\frac{ppm\ He \cdot 10^{-6} \cdot P_c}{{}^{1}K_{He}} \cdot \frac{V_w}{18.01} \right] \right] \cdot \left[1 - \frac{1}{1 + \frac{RT_f V_w}{V_p\ {}^{f}K_{He} \cdot 18.01}} \right] \right\} \cdot \frac{22414}{V_w} \qquad (99)$$

where

ppm He = Reported value for helium concentration in the headspace of a sample (absolute)

Again, terms that appear in (99) have the same definitions and units that are given in table 1.

As previously, if temperatures are input as ^{o}C (instead of ^{o}K) the following correction must be made:

$$\frac{cc\ He}{cc\ H_2O} = \left\{ \left[\frac{273.16}{22414} \cdot \left[\frac{ppm\ He \cdot 10^{-6} \cdot P_c}{({}^{c}T_1 + 273.16)} (V_h + V_p) - \frac{5.24 \cdot 10^{-6} \cdot V_h\ P_f}{({}^{c}T_f + 273.16)} \right] + \left[\frac{ppmHe \cdot 10^{-6} \cdot P_c \cdot V_w}{{}^{1}K_{He} \quad 18.01} \right] \right] \cdot \left[1 - \frac{1}{1 + \frac{R \cdot ({}^{c}T_f + 273.16) \cdot V_w}{V_p \cdot {}^{f}K_{He} \cdot 18.01}} \right] \right\} \cdot \frac{22414}{V_w} \qquad (100)$$

where

${}^{c}T_f$ = Temperature of soil at time of collection in ^{o}C

${}^{c}T_1$ = Temperature of sample at time of analysis in ^{o}C

Again, pressures and Henry's law constants should be in terms of units of atmospheres. With this in mind, equation (100) represents the final equation for calculating the concentration of helium in the moisture of a soil sample using measured values of helium in the headspace above the soil.

It is important remember that both equations for calculating the actual concentration of helium in a soil sample, whether as volumes of He per volumes of pore space or volumes of He per volumes of water, would yield equivalent results since each quantity is dependent on the other, and that the choice of which to use -(93) or (100)- would depend on the composition of the sample.

Helium in Totally Wet Soils and Water Samples

For a sample totally composed of soil and water with no gaseous pore space, or of water only, excess helium measured in the headspace over the sample is entirely due to the exsolution of helium dissolved in the water of the sample. An equation can be derived to calculate the concentration of helium that existed in the sample at the time of collection using the helium in headspace concentration. This equation is essentially a subset of the previous derivation for helium in pore space concentrations in that when the volume of gaseous pore space becomes nonexistant (i.e. zero), parts of the derived equations that pertain to helium in porespace would also become equal to zero.

Taking equation (100)--the final equation for calculating the concentration of helium in moisture of a soil sample--and setting the volume of gaseous porespace, V_p, equal to zero yields:

$$\frac{\text{cc He}}{\text{cc } H_2O} = \left[\frac{273.16}{22414} \cdot \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{({}^cT_l + 273.16)} \cdot V_h - \frac{5.24 \cdot 10^{-6} V_h P_f}{({}^cT_f + 273.16)}\right.\right.$$

$$\left.\left. + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c \cdot V_w}{{}^1K_{He} \cdot 18.01}\right]\right]\right] \cdot \frac{22414}{V_w} \qquad (101)$$

Simplifying (101):

$$\frac{cc\ He}{cc\ H_2O} = \frac{273.16}{V_w}\left[\frac{ppm\ He \cdot 10^{-6} \cdot P_c}{({}^{c}T_1 + 273.16)} \cdot V_h - \frac{5.24 \cdot 10^{-6}\ V_h P_f}{({}^{c}T_f + 273.16)}\right]$$

$$+ \frac{ppm\ He \cdot 10^{-6} \cdot 22414 \cdot P_c}{{}^{1}K_{He} \cdot 18.01} \qquad (102)$$

Equation (102) is the final expression for calculating the absolute concentration of helium originally present in a water sample or totally wet soil samples using measured values of helium in the headspace of a sample container. It should be emphasized that this equation is only valid if the units of measurement are the same as those used in this derivation.

The above sections have presented the derivation of three equations for calculating what the original concentrations of helium in gaseous pore space of a soil sample, in the moisture of a soil sample, or in the moisture of a totally wet soil or water sample, must have been to yield the analyzed concentration of helium in headspace from a sample container. The appropriate equation number to use for a given sample type is shown in table 2.

These equations give the concentrations of helium present in a sample under STP conditions. Due to the nature of ideal gas behavoir, it can be assumed that concentrations calculated at STP conditions are equivalent to concentrations of helium at other conditions of temperature and pressure, i.e. field conditions.

Table 2. Equations of use for calculating helium concentrations in varying types of samples.

Sample	Equation No.	Concentration units
Soil -- dry to moderately wet	93	cc He/cc gaseous pore space
Soil - wet	100	cc He/cc H_2O
Soil -- totally wet, no gaseous pore space	102	cc He/cc H_2O
Water	102	cc He/cc H_2O

Dilution By Overpressuring

When a sample's contained pressure was lower than that of the laboratory, gas for analysis could not be directly withdrawn. Therefore, 5 (or occasionally 10) cc's of ambient air was added to overpressurize the Vacutainers of the Long Valley samples and allow the removal of a gaseous sample. This dilutes the helium in the sample and a correction for this procedure must be done to obtain an accurate determination of the actual helium concentration existing in a sample.

The question arises as to whether this added air undergoes any equilibration with the gaseous pore space in a soil sample in addition to equilibration with the gaseous headspace. The degree of equilibration with the pore space would depend on the sample type.

Clays. With vigorous vortex stirring after addition of the air, it is probably valid to assume that equilibration between the added air and the gaseous headspace of the sample occurs quickly. The concentration of helium that existed in the headspace of the sample prior to this dilution can be calculated from the following:

$$[He]_{corr} = \frac{(He)_{meas}\,(V_h + V_a) - 5.240\,V_a}{V_h} \qquad (103)$$

assuming 100% equilibration between added air and headspace volume where

V_h = the amount of gaseous headspace in the sample container (cc)

V_a = the amount of air added to overpressurize the sample container (cc)

$[He]_{meas}$ = the absolute concentration of helium measured in the sample (ppm)

$[He]_{corr}$ = the absolute concentration of helium in the sample corrected for dilution (ppm)

5.240 = the concentration of helium in air (ppm)

For a clayey sample equilibration with the pore space would be minimal in the elapsed period of time between addition of the excess air and analysis, due to limited accessibility of the pore space headspace gas. Therefore, the concentration of helium existing in the headspace prior to dilution could be calculated by assuming only equilibration between helium in the added air and helium in the gaseous headspace as in equation (103). This would also be the case with wet clays since the amount of gaseous porespace in such a sample is very small.

Sands. Since the majority of samples taken in Long Valley were loose (unconsolidated), sandy soils and low in moisture content, the addition of added air with vigorous stirring suggests that a high degree of equilibration between helium in the added air, helium in the gaseous headspace of the container, and helium in the gaseous pore space of the sample occurs. For treatment of the data, the degree of equilibration between the added air and the gaseous pore space was assumed to be 100%. Therefore, the amount of helium measured in the headspace can be corrected to the concentration of helium in the headspace that existed prior to dilution with the added air by the following calculation:

$$[He]_{corr} = \frac{(He)_{meas}\,(V_h + V_a + V_p) - 5240\,V_a}{V_h + V_p} \qquad (104)$$

assuming 100% equilibration between the added air and the gaseous headspace and porespace.

where

V_p = the amount of gaseous pore space in the sample (cc's)

It must be remembered that the degree of equilibration between the added air and the gaseous porespace of a sample could easily vary depending on the sample. Thus, the actual concentration of helium existing in the sample prior to dilution could lie between the number calculated by assuming equilibration with only the headspace volume (0% equilibration with the pore space) and the number calculated by assuming equilibration with the headspace and the pore space volumes (100% equilibration with pore space). This problem caused by varying amounts of equilibration between the added air and the sample could be avoided by adding the air after collection but prior to the equilibration period.

The Long Valley helium in headspace concentrations were corrected for the dilution caused by the addition of air using equation (104).

Tables of the amount of air added to the Long Valley samples, the measured helium in headspace concentrations, headspace concentrations corrected for dilution (by equation (104)),and the difference in concentration as a result of this calculation are presented in Appendix B.

The dry soils of Long Valley were found to contain significant amounts (often greater than 40%) of gaseous pore space. Therefore, it was decided to calculate the concentration of helium in the samples by the use of equation (93). This yielded helium concentrations as ppb of He in gaseous pore space.

EVALUATION OF VACUTAINERS AS SAMPLE CONTAINERS

Helium, due to its small molecular size, can rapidly diffuse through matter. Containers chosen to collect samples of soil, soil gas or water should have a low leakage rate for helium over the period of time that the samples are to remain in the container before removal for analysis. Expense, practicality, accessibility and ease of shipping are also important considerations in choosing sample containers.

For both the Fiji and Long Valley surveys, Vacutainer brand evacuated blood collection tubes were used for sample collection. These are made of glass with an butyl rubber septum and are manufactured by Becton-Dickinson, Rutherford, New Jersey. Expiration dates, sterility information, and lot numbers are given on each package. Nonsterile, 10 ml or 20 ml Vacutainers with no additive or internal coatings were used in these studies. These tubes are received evacuated to about 1/5 atmosphere. After collection of a soil sample, silicone rubber sealant was applied around the edge of the rubber stopper to help prevent loss of gas.

A study to ascertain the degree of leakage of helium out of Vacutainers was done. Leakage could occur by diffusion through the glass of the tube, diffusion through the rubber of the stopper, or around the seal of the rubber stopper and the glass tube.

On 11/10/82, thirty 10 ml Vacutainers were filled with outside air-5240 ppb He in concentration--by injecting 11 cc into the tube. The small hole created in the stopper was covered with silicone sealant. Thirty additional Vacutainers were filled with a reference gas containing an 8200 ppb mixture of helium in air, and thirty more were filled with a 5874 ppb reference gas mixture. These were also sealed with silicone. Five samples of each concentration of gas were periodically analyzed for helium content over a period of 54 days. Results are presented in table 3.

Results were graphically depicted by plotting the mean of each set of data versus the date of analysis, as shown in figure 10. Error bars for each point were determined by calculating the amount of error inherent in reading the strip chart record in determining helium content (+/- 0.25 division)), and adding twice the standard deviation (two sigma) to each data set. The usage of two sigma should take into

Table 3. Vacutainer Tests--Variations in Helium Concentrations with Time.

Analysis Date	5240ppb (air)	5874ppb	8200ppb
11/10/82	6040	6448	
	6026	6444	8164
	6173	6466	8216
	6182	6555	8145
	6040	6408	8141
Mean +/- Std. dev.	6092 +/-78	6464 +/-55	8167 +/-34
11/12/82		6585	
	6196	6450	
	6166	6450	8410
	6106	6585	8352
	6076	6604	8448
Mean +/- Std. dev.	6136 +/-55	6535 +/-78	8403 +/-48
11/22/82	6230	6856	
	6296	6839	8958
	6345	6790	8853
	6230	6856	8909
	6213	6873	8993
Mean +/- Std. dev.	6263 +/-56	6843 +/-32	8928 +/-61
12/6/82	6215	6508	8090
	6079	6625	8090
	6099	6465	8206
	6099	6567	8206
	6099	6586	8206
Mean +/- Std. dev.	6094 +/-10	6550 +/-64	8160 +/-64
12/16/82	5902	6272	
	5906	6452	8023
	5902	6511	8113
	5864	6228	8068
Mean +/- Std. dev.	5894 +/-20	6366 +/-137	8068 +/-45
1/3/82	6112		7872
	6047		8013
	6112	6452	8013
	6099	6635	8060
	6047	6635	8060
Mean +/- Std. dev.	6083 +/-34	6574 +/-106	8004 +/-77

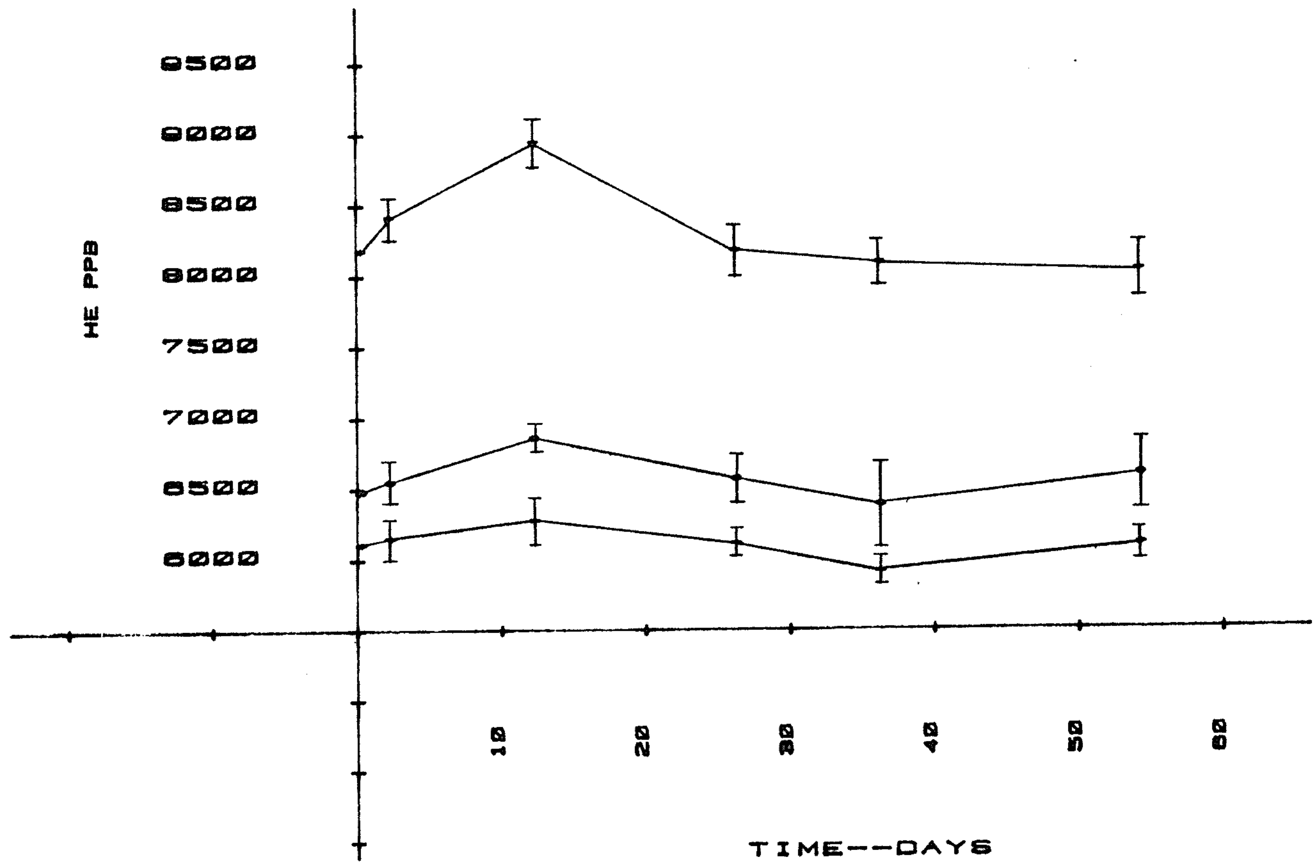

Figure 10. Graph of leakage test results over time.

account variations among the Vacutainers (such as residual helium contents) for 97.5% of all samples based on the number of measurements taken at each point.

After filling of Vacutainers with air or reference gas "instantaneous" analyses done 20 minutes after filling (day 0) showed a marked increase in helium from the injected concentration of gas for the sets filled with air (5240 ppb to 6092 ppb) and the 5874 ppb reference (5874 ppb to 6464 ppb), and a slight decrease for the set filled with the 8200 ppb reference (8200 ppb to 8167 ppb). A rise in helium concentrations is then observed for all three sets up until at least day 12, followed by a decrease in helium concentrations subsequently.

It is proposed that these results are due to the preferential leakage of helium into the reduced pressure atmosphere of the evacuated Vacutainers prior to filling. If this residual gas was of a higher concentration than that added to the tube, a rise in the measured helium concentration could be expected. This can be supported by calculating the helium concentration that must have existed in the tubes at the time of filling due to leakage of helium into the evacuated Vacutainers. It was found that for each gas mixture--5240, 5874, and 8200 ppb-the calculated amounts of residual helium, within experimental error, were the same. The helium concentration existing in the Vacutainer at the time of filling due to leakage into the tubes was calculated by:

$$[He]_{res.} = \frac{[He]_{meas.}\,(V_{res.} + V_a) - ([He]_{ab.}\,V_a)}{V_{res.}} \quad (105)$$

where

$[He]_{meas.}$ = the concentration of helium measured in the Vacutainer immediately after filling.

$V_{res.}$ = the volume of gas that existed in the evacuated tube prior to analysis at room temperature and pressure

V_a = the volume of gas mixture containing helium that was injected into the tube

$[He]_{ab.}$ = the absolute concentration of the helium mixture that was injected into the tube

and

$[He]_{res.}$ = the concentration of helium that existed in the Vacutainer prior to filling

It was determined that a nominal 10 ml Vacutainer had an actual volume of approximately 12.5 ml, and that most Vacutainers contained residual volumes after manufacturer evacuation of 3.0 cc +/- approximately 0.3 cc. Error estimates in the usage of the above equation were made by assuming the following:

$V_{res.}$ = 3.0 +/-0.3 cc, due to variations in the evacuation of tubes, etc.

V_a = 11.0 +/-0.1 cc, due to errors in filling

$[He]_{meas.}$ = mean concentration +/-2 std. dev.

For an injected helium gas mixture of 5240 ppb concentration (air), the residual helium concentration in the tube was calculated to be 9216 +/- 2779 ppb. The 5874 ppb reference yielded a residual helium concentration of 8627 +/-2588 ppb, and the higher reference gas containing 8200 ppb yielded a calculated residual concentration of 8046 +/-2680 ppb. Within the estimates of error, it can be seen that these results yielded the same value for the concentration of helium existing in Vacutainers prior to filling, and that this concentration is higher than the 5240 and 5874 gas mixtures and approximately the same as the 8200 reference gas. This tends to support the hypothesis that the initial increase in the concentration of helium observed after filling is due to contamination with residual helium in the Vacutainer.

It would be expected that the concentration of helium in a filled sample container would decrease due to outwards leakage if the contained concentration of helium is greater than that of helium's concentration in air. The observed pattern of such leakage versus time can be expected to follow an exponential decay curve, eventually reaching a plateau when equilibration with the atmospheric concentration of helium was achieved. The period of time during which this equilibration occurs would be the measure of a container's resistance to helium leakage. Results in this study do not show an immediate decrease after filling, but rather continued increase in the helium concentration up to at least 12 days after filling. It has already been suggested that the initial increase in helium concentrations that is observed is due to the presence of high concentration residual helium. But this would not account for the continued observance of concentration increases. It is suggested that prior to a Vacutainer's filling with a sample, the pore spaces or surface of the butyl rubber stopper, and to less degree possibly pore spaces within the glass of the Vacutainer, would contain helium in equilibrium with the higher concentration of helium in an evacuated tube. The observed increase in helium after injection may then be due to an outgassing of these higher concentrations of helium in the rubber stoppers (and glass) that is then mixing with the helium present in the tubes. Under such a mechanism the measured concentration of helium would increase until equilibration with the helium of the stoppers is achieved.

After the analyses done on day 12 (Nov. 22), within experimental errors, the measured helium concentrations show a steady decrease for the various gas mixtures over the remaining 54 day period. This would undoubtably be due to the leakage of helium out of Vacutainers. This leakage would continue until equilibration between the helium in the tube and the atmosphere was eventually achieved at a helium concentration of 5240 ppb.

In conclusion, it can be suggested that the observed pattern (as represented in Figure 10) of changes in helium concentrations within the Vacutainers of this study are due to initial mixing of high concentration residual helium with the injected gas mixture, additional mixing of higher helium present in the rubber stopper with the contained mixture, and finally, diffusion of helium out of the Vacutainers.

An apparent leakage rate for helium out of the Vacutainers of this study can be calculated by examining the difference between the initial concentration of helium measured on day 0, and the final concentration of helium measured on day 54. The series of tubes filled with 5240 ppb (air) of helium yielded a mean concentration of 6092 ppb upon filling and a value of 6083 ppb after 54 days, or a loss of 9 ppb in 54 days. This would equal a 0.01% loss of excess helium. The series of Vacutainers filled with 8200 ppb yielded an initial mean concentration of 8167 and a final concentration of 8004 ppb. This would equal a 0.06% loss of excess helium. The series filled with 5874 ppb helium showed a gain of 110 ppb, from a mean of 6464 to 6574 ppb. This may be a result of poor standardization.

The leakage observable in this study is well within experimental errors of the study. Note that this is apparent leakage and represents actual leakage of helium out of the Vacutainers occurring concurrently with outgassing of high concentration helium in the rubber stoppers. Thus, actual leakage and high helium outgassing have cancelling effects on each other.

For the Fiji and Long Valley helium surveys the preferential leakage of helium and other gases into an evacuated Vacutainer prior to filling with a sample is not a concern since tubes are uncapped for a short period of time before a soil sample is collected allowing flushing of the container. Therefore, an initial "instantaneous" increase in the helium concentration due to residual helium would not have occured. The outgassing of high concentrations of helium in the rubber stoppers probably did occur, as would concurrent leakage out of Vacutainers. Thus, for these two surveys, an observed pattern of flucuations in helium concentrations within Vacutainers over time may be similar to that of the above study (figure 10). Initial concentrations should not show an increase due to mixing with residual helium, but a gradual rise in the helium might still occur over an initial period of time, followed by a gradual decrease in helium concentrations as leakage begins to have a greater effect. Again, depending on the amount of elapsed time between collection and analysis, the leakage over the time period that occurs prior to analysis for both studies may be insignificant due to the cancelling effects of outgassing and leakage.

Samples collected in Long Valley were analyzed two and a half weeks after collection, and Fiji samples were analyzed between a minimum time of three weeks after collection, and a maximum time of 8 weeks after collection. Based on results presented here, the range of time between collection and analysis of the Long Valley and Fiji samples was considered to fall after significant increases in helium concentrations has occured due to degassing of helium in the stopper, but before significant amounts of leakage occur (i.e. the net helium concentrations are relatively unchanged). If this is true, no correction for leakage into and out of the Vacutainers used in the Long Valley and Fiji survey need be done and errors associated with this pheonomenon should be minimal.

Extreme caution seems indicated in using Vacutainers as collection containers for helium surveys as there seem to be many considerations when evaluating their leakage potential. The degree of evacuation and the amount of time that elapses before the evacuated tubes are used would seem to have a large effect on leakage rates. If analysis is done soon after sample collection, the effect of helium outgassing (from stoppers) may have a marked effect on the measured values giving concentrations higher than actual. If analysis of samples is not done till several months after collection, results may give helium concentrations that are too low, due to loss by leakage.

The many sources of variations in using Vacutainers suggest alternate containers might be more suitable, especially for studies where precision is important or where samples may not be analyzed soon after collection.

RESULTS

It was discovered in the calculation of the concentration of helium in gaseous pore space (equation (93)) that samples with only a small amount of measured pore space gave rise to calculated helium concentrations that were suspect. This is due to nature of the calculation, and inherent errors taking on a greater magnitude of effect at low values of gaseous pore space. For the Long Valley survey, results on samples with measured volumes of gaseous pore space of less than 1.0 cc were considered questionable. Out of the 212 soil samples collected, 8 (<4%) had pore space volumes of less than 1.0 cc.

These samples were not considered in the interpretation of helium in pore space data.

Concentrations of helium in the headspace of the Long Valley soil samples, uncorrected for any parameters, ranged from -208 to 562 ppb helium in excess of helium in ambient air. The mean and standard deviation of the 212 samples was 82 +/- 112 ppb He. A frequency distribution plot of the data is given as figure 11. Results are depicted as a contour map of helium concentrations shown in figure 12. Contouring of the data was done using a computer program written for the Hewlett Packard 9825A desktop computer (Reimer and Dean, 1979). This contouring program allows for a smoothing of data by nearest neighbors weighted inversely by the square of the distance to the neighboring samples.

Concentrations of helium in the gaseous pore space of the soil samples calculated using equation (93) ranged from -400 to 2500 ppb helium in excess of helium in ambient air. The mean and standard deviation of the samples was 688 +/- 1075 ppb He. These results show a skewing towards the high side. A frequency distribution plot of the data is given in figure 13. A contour map of the calculated helium concentrations is presented in figure 14.

Negative values relative to the concentration of helium in air, 5240 ppb, are observed for the helium in headspace and the calculated helium in pore space data. It should be pointed out that this is caused by the dilution of helium in a soil by other gases such as

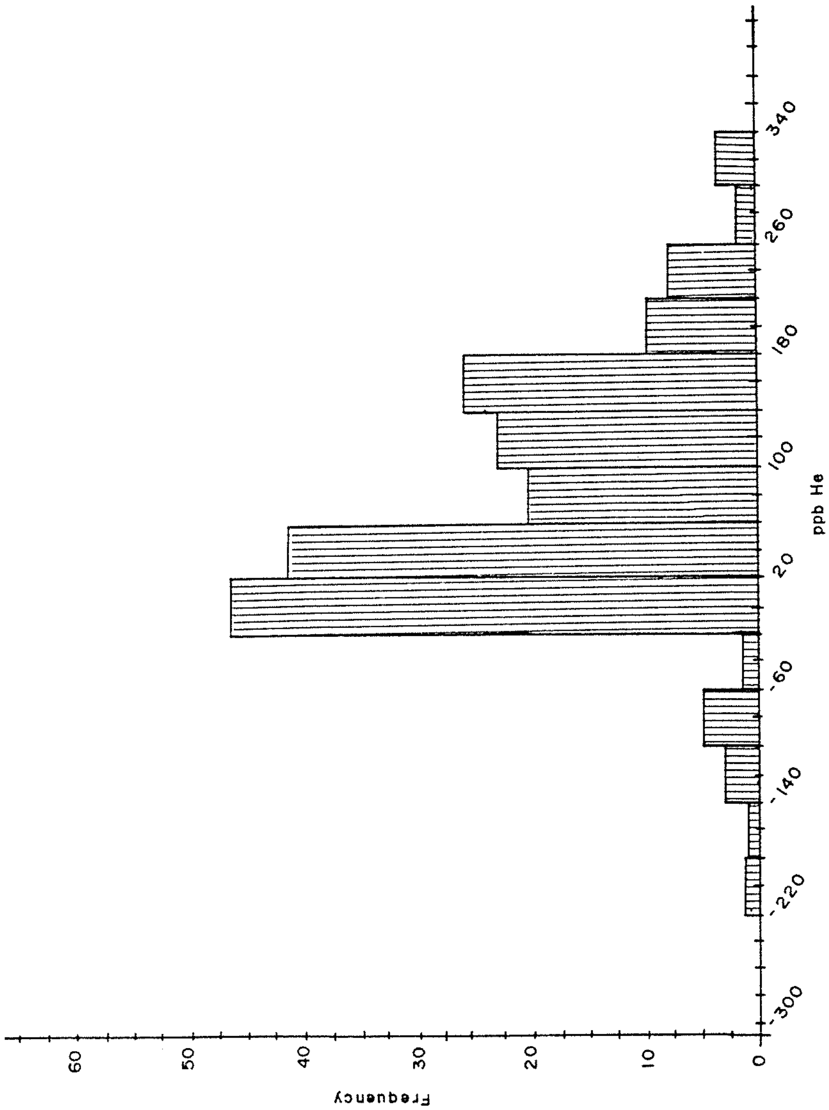

Figure 11. Frequency diagram of uncorrected helium in head-space concentrations for the Long Valley area.

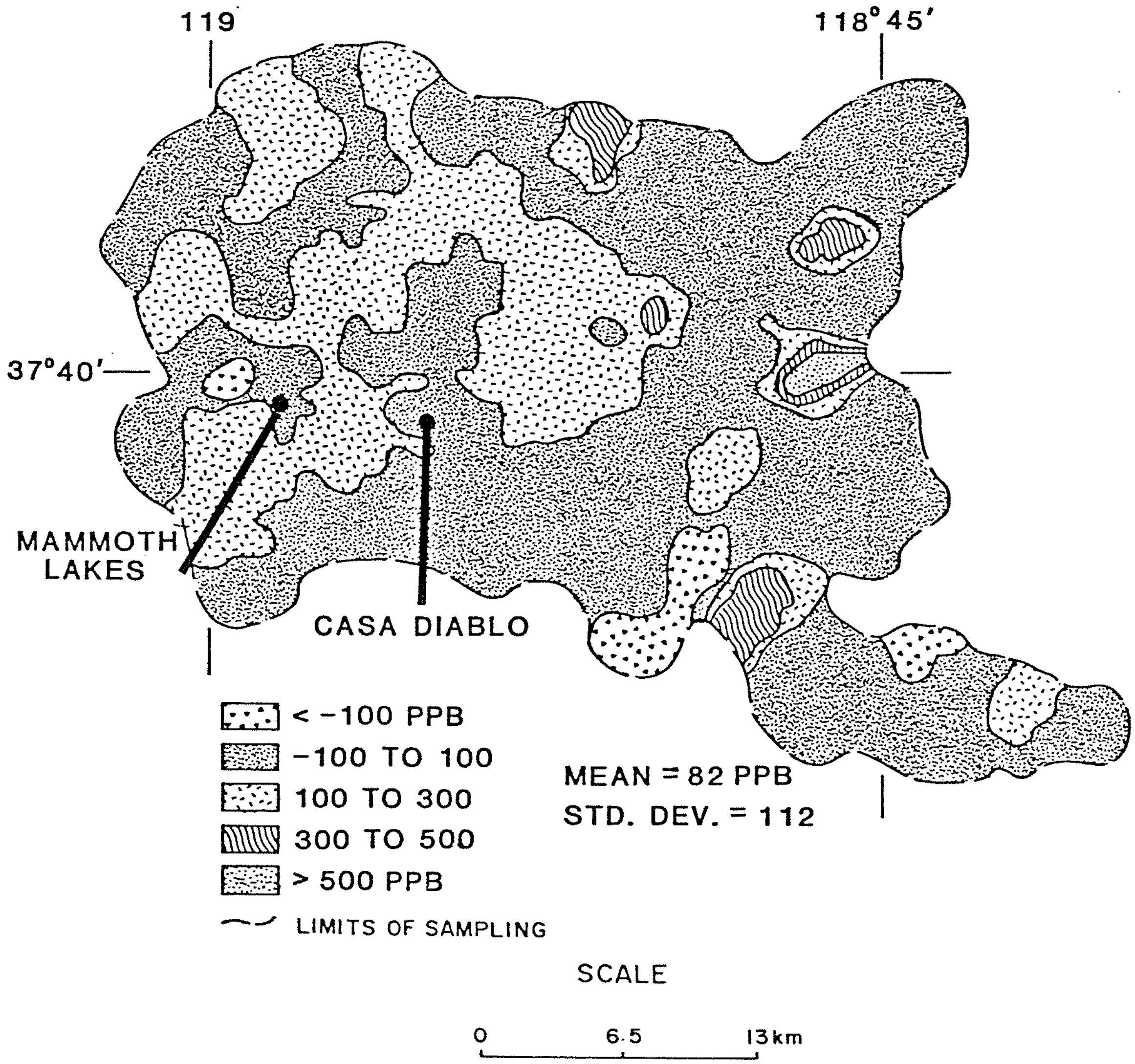

Figure 12. Smoothed contour map of uncorrected helium in headspace concentrations for the Long Valley area.

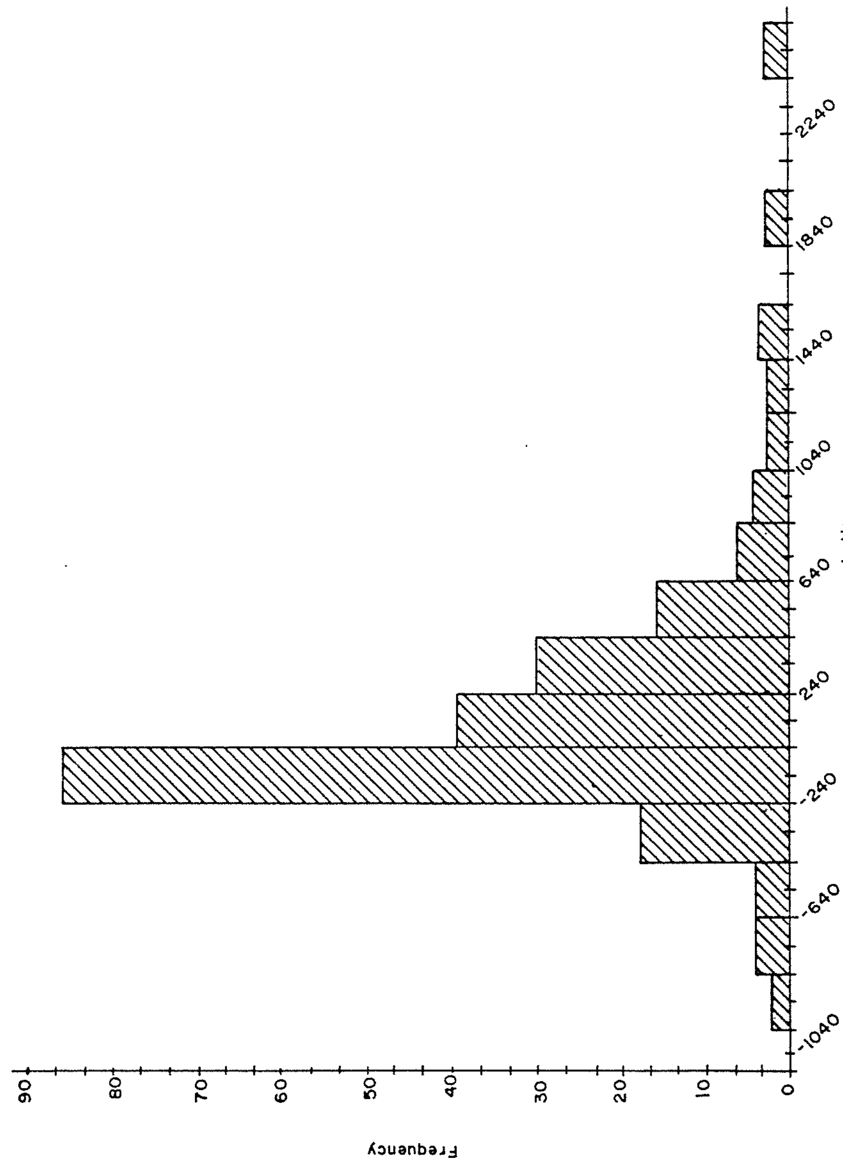

Figure 13. Frequency diagram of calculated helium in gaseous soil pore space concentrations, Long Valley.

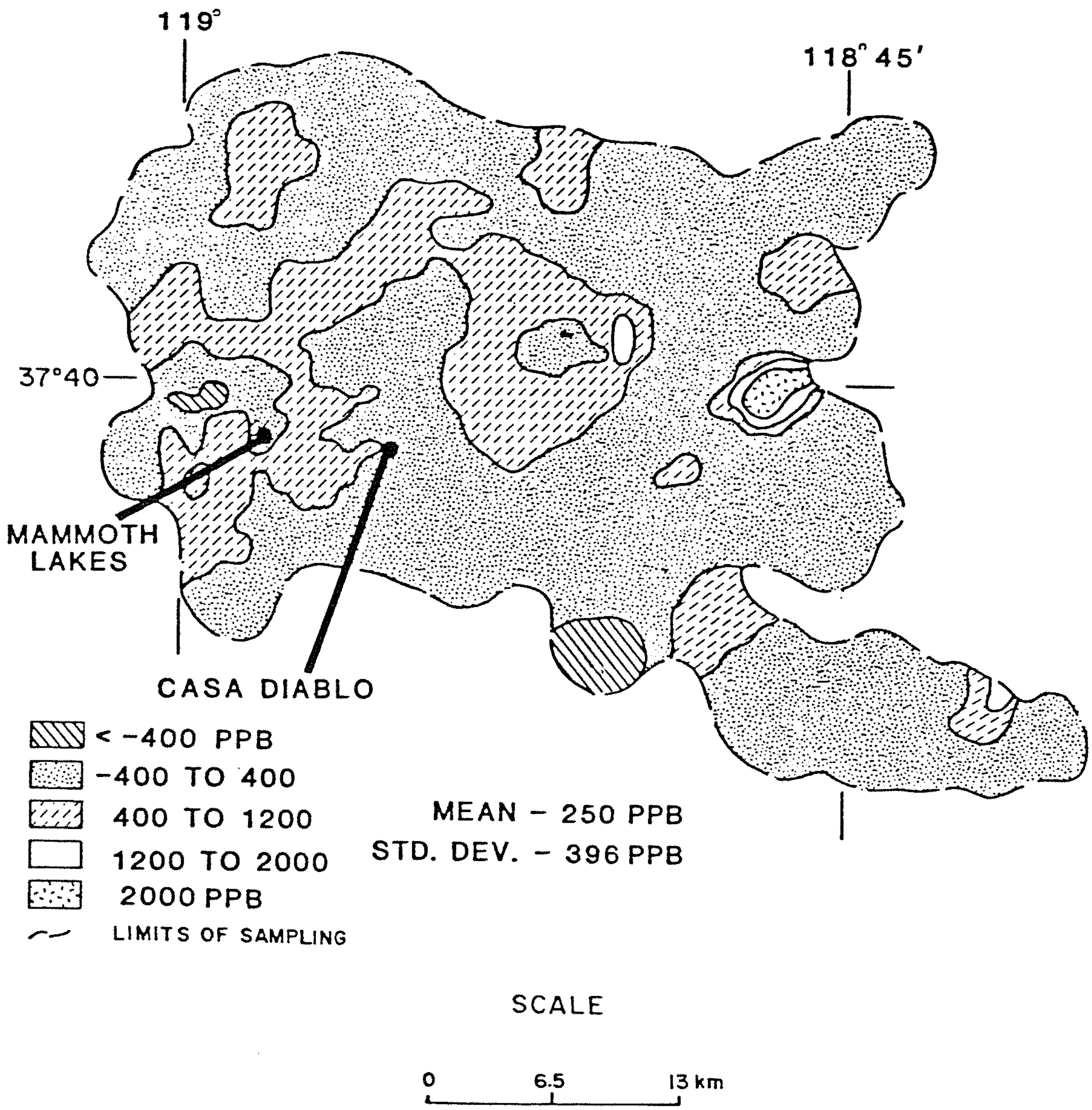

Figure 14. Smoothed contour map of helium in gaseous soil pore space concentrations for the Long Valley, area.

carbon dioxide, water vapor, methane, and hydrogen.

Appendix B contains tabulated data on each soil sample collected in Long Valley, including volumes of pore space, headspace, and water, field temperature and pressure, canned pressure, helium in headspace and helium in pore space.

Before conclusions were drawn from these results, an examination of the variables or parameters that occur in the calculation of helium in gaseous pore space was conducted. This is presented in the following section. From this analysis, parameters that significantly affect the helium concentration were identified, and an estimation of the amount of error associated with these determinations was made.

EXAMINATION OF PARAMETER VARIATIONS AND ERRORS

The variables that occur in the equation for calculating the helium in gaseous pore space concentration (equation (93)) are listed in table 4. Definitions are the same as those in table 1. Using measurements made in Long Valley, these variables were examined to identify the parameters which seem to have the greatest effect on the determination of the concentration of helium in the gaseous pore space of soil samples. Parameters found to produce a large amount of variation in the calculated helium in pore space values would be of greater importance to measure accurately. Additionally, an estimation of the amount of error associated with a typical helium in pore space concentration for the Long Valley survey was made by examining errors

Table 4. Variables that Occur in the Calculation of He in Porespace Concentrations by Equation (93).

V_w	P_f	T_1
V_h	P_c	${}^{1}K_{He}$
V_p	T_f	${}^{f}K_{He}$

related to individual variables or parameters. This yielded an approximation of confidence limits for the Long Valley data.

Effects of Parameter Variations. Typical variations among parameters that were directly measured in the Long Valley survey were used to identify those that seem to have a greater significance in the determination of actual helium in soil concentrations. The variables that were examined included the volume of soil pore space, volume of soil moisture, volume of sample headspace, soil temperature, and field barometric pressure. Using equation (93) and the mean helium in headspace concentration for the Long Valley samples of 5322 ppb, components of the equation were varied individually and the resultant helium in pore space concentration calculated. Results are presented in table 5, and discussed below.

Table 5. Resultant Differences in Calculated Helium in Gaseous Pore Space Concentrations due to Variations within the Long Valley Survey.

Variable	[He] in Porespace Condition 1	[He] in Porespace Condition 2	Difference (ppb)
V_p	10% = 5623	50% = 5383	240
V_h	15% = 5361	40% = 5427	66
V_w	1% = 5392.1	12% = 5392.2	0.1
T_f	$5^{\circ}C$ = 5392.0	$25^{\circ}C$ = 5392.1	0.1
P_f	0.75 atm = 5392.1	0.79 atm = 5392.1	0.0

Gaseous porosity or pore space in a soil sample constituted between 10 to 50% of the total soil volume for most of the Long Valley samples. Using 10% of an average soil volume (1.6 cc) as the volume of gaseous pore space, 5322 ppb as the helium in headspace concentration, and mean values for the other variables, a calculated helium in pore space concentration of 5623 ppb is obtained. Using an average gaseous pore space volume of 50%, a helium in headspace concentration of 5322 ppb, and the same values for the other variables yields a calculated helium in pore space concentration of 5383 ppb. This range in pore space yields values for the calculated helium in porespace that differ by 240 ppb. But each sample would have the same spectrometrically measured helium in headspace value of 5322 ppb. This suggests that gaseous pore space volumes may be a fairly critical parameter to carefully measure for an accurate determination of helium in pore space concentrations. As would be expected, the calculated concentration of helium in pore space is an inverse function of the amount of gaseous pore pace.

Volumes measured for the headspace of the Long Valley samples typically ranged from 15% to 40% of the total volume (22 cc) of the sample container, or Vacutainer. A headspace value of 15% (3.3 cc) would yield a concentration of 5361 ppb for the concentration of helium in the soil pore space, and 5427 ppb for a sample with a headspace value of 40% (8.8 cc). This represents a difference of 66 ppb between the calculated helium in pore space concentrations due to variations in the amount of headspace. This suggests that, while not as significant as the measurement of gaseous pore space, it would be important in the calculation of helium concentrations to accurately measure the volume of headspace in a sample container. A larger amount of headspace in a sample container would cause additional dilution of the helium in a soil by atmospheric concentrations of helium. This would result in original concentrations of helium, when calculated, that would be higher than that of a helium sample with a smaller headspace volume. This is indicated by the above results which show the concentration of helium in pore space to be a direct function of the headspace parameter.

For the arid soils of Long Valley, a typical range in the amount of soil moisture is 1 to 12% of the total sample volume for most of the collected samples. An average soil with 1% of moisture (0.16 cc), would yield a helium in pore space value of 5392.1 ppb, while the same soil sample with 12% of moisture (1.92 cc) would give a value of 5392.2 ppb--a difference of only 0.1 ppb. This indicates that variations in soil moisture of the above magnitude have very little effect in the determination of helium in pore space concentrations. These results are logical when helium's low solubility in water is considered. If the pore space in a soil sample is totally, or almost totally, composed of water, this parameter will become important. Note that for two soils with the same amount of gaseous pore space but differing amounts of water, soil moisture has a direct relationship to the calculated helium concentrations--the helium in pore space concentrations increase slightly as the amount of soil moisture increases.

For a range of 5°C to 25°C in the field soil temperatures within the survey, a difference of only 0.1 ppb is observed between the calculated helium in pore space concentrations. A soil temperature of 5°C would yield a concentration of 5392.0 ppb helium in pore space and 25°C would give a concentration of 5392.1 ppb helium in pore space. Soil temperature does not seem to have a large effect in the determination of helium in pore space concentrations when compared to other parameters. While it is not of great magnitude, it can be noted that calculated helium in pore space concentrations are a direct function of soil temperatures.

The examination of barometric pressures measured under field conditions in Long Valley showed a range of 0.04 atm, from 0.75 atm to 0.79 atm, for a majority of the samples. Using a pressure of 0.75 atm and means for the other variables gives a helium in pore space concentration of 5392.1 ppb. A helium in pore space concentration of 5392.1 ppb is also obtained using a pressure of 0.79 atm. No difference is incurred when changing the pressure in the calculation of helium in pore space concentrations by equation (93). This result is an artifact of the calculation and the fact that pressures inside the sample containers (P_c) were not actually measured, but calculated using the thermodynamic relations between field and laboratory barometric pressures and temperatures. The subsequent correction of field pressures and container pressures back to STP conditions within the helium in pore space equation, creates a cancelling or counter-balancing effect. Using the field pressure and the gas law to calculate container pressure, equation (93) can be reduced to an expression that does not contain pressure terms. The measurement of P_f and P_c will not make a difference in the calculation of helium in pore space concentrations unless the variation between container pressure and field pressure differs from what would be thermadynamically predicted. For accurate results both container pressures and field barometric pressures should be measured and used in the calculation of corrected helium concentrations.

These results suggest that, at least for the Long Valley survey, variations in gaseous pore space, and to a lesser degree, headspace volumes have a significant effect on the calculated concentration of helium in soils, and that soil moisture and soil temperature may exert lesser effects. Therefore, for an accurate determination of the concentration of helium in gaseous soil porespace, an accurate measurement of pore space and headspace volumes are needed, but a degree of error in the other parameters may not be as significant. This examination also indicates that, depending on the size of detectable anomalies, the use of helium in headspace concentrations may not be a valid indicator of the pattern of helium anomalies in an area. This is illustrated by the observation that while two samples may exhibit the same measured helium in headspace value (such as the mean value used here of 5322 ppb), the actual helium concentrations in the samples may be extremely different if, for example, the gaseous pore space volumes differ significantly between the two.

Evaluation of Parameter Errors

It would be useful to determine the amount of error associated with the measurement and calculation of the Long Valley helium in pore space concentration. This was done by taking average or mean values for the variables, including a mean helium in headspace value of 5322 ppb, and calculating the resultant helium in gaseous pore space concentration--5392 ppb. Then an estimation of the amount of error associated with each variable was made. Each variable in the equation for calculating the amount of helium in gaseous pore space was then allowed to vary by the estimated amount of error, and new helium in pore space concentrations were calculated. The difference between the mean helium in pore space concentration and the concentration obtained by varying individual parameters according to error estimates was recorded. Finally, the resultant differences in the helium in pore space concentration calculated by the evaluation of errors were combined to give an overall estimation of the error associated with the mean helium in gaseous pore space value of 5392 ppb. Results are presented in Table 6 and discussed below.

Table 6. Differences from the Mean Calculated Helium in Pore Space Concentration (5322 ppb) Caused by Error Estimates for the Long Valley Study.

Variable	Mean of Variable	Error Estimate	Difference from Mean--ppb
T_f	16^oC	+/- 1.0^oC	+/- 0.1
P_f	0.77 atm	+/- $3.3.10^{-3}$ atm	0.0
V_p	6.9 cc	+/- 0.5 cc	+/- 6
V_w	0.82 cc	+/- 0.25 cc	+/- 0.1
V_w	0.82 cc	+/- .007 cc	+/- 0.0
V_h	5.9 cc	+/- 1.0 cc	+/- 12.0
V_h	5.9 cc	+/- 0.15 cc	+/- 2.0
T_l	30^oC	$-1/0^oC$	+/- 0.0
P_c	0.80 atm	+/- .001 atm	+/- 12
K_{He}	1.4375x105	+/- 0.4 x 10^5 mol H_2O/mol He	+/- .2
$[He]_{hdsp}$	5322 ppb	+/- 20 ppb	+/- 36

Total Error Estimate = +/- 40.3 ppb

Soil Temperature-Field. Soil thermometers used in the Long Valley survey could be accurately read to the nearest 0.5^{o} degree centigrade, introducing a possible error of $+/-0.5^{o}C$ in the measured soil temperature. Since the temperature is not taken at the exact sampling site, but 6" to 1' away and at the approximate depth of sample collection, it is possible that this would introduce additional variation in the temperature measurement. This variation was considered to be on the order of $+/-0.5^{o}C$. Summing these would give a possible total variation in the accuracy of the soil temperature measurement of $+/-1.0^{o}C$. Using this variation in the helium in pore space calculation yields a helium in pore space concentration of 5392.2 ppb with an increase of one degree, and a concentration of 5392.1 ppb with a decrease of one degree. The average difference from the mean helium in porespace value--5392.1 ppb--would be less than +/-0.1 ppb.

Barometric Pressure-Field. A typical error associated with reading the altimeters used for pressure determinations in the Long Valley survey would be about 3.3×10^{-3} atm (+/-0.1 inch of Hg). Changing the mean of the pressure measurements made in Long Valley--0.77 atms--by $+/-3.3 \times 10^{-3}$ atm yields calculated helium in porespace concentrations that do not differ from the mean 5392 ppb concentration. Again this is due to the calculation of container pressures having a cancelling effect on the differences due to field pressure variations. This variation can have a significant effect if the container pressure is also measured to compensate for gas production or consumption.

Gaseous Pore Space. Errors in the values determined for the amount of gaseous porespace in a soil sample could result from a number of sources. If incomplete evacuation of a sample occurred during the measurement of gaseous soil pore space, the resultant values for the amount of pore space would be smaller than the actual values. Soil types such as clays might exhibit this problem as their pore space would be less amenable to measurement by this technique, due to low permeability of such soils. Significant error associated with incomplete evacuation were assumed not to exist for the Long Valley samples, as all were fairly dry and contained loose (unconsolidated), nonclayey soils. An error estimate would also include the accuracy of reading the syringe used to measure the amount of air drawn in after sample evacuation. The syringe can be read to the nearest 0.5 cc. Introducing a possible variation of +/-0.5 cc would give calculated helium in pore space values that differ from the mean by +/-6.0 ppb. Possible errors could also result from the disturbance of the soil sample that occurs during transfer from the ground to the sample container. It may be that this significantly disrupts the porosity of the soil, thus being reflected in the measured value for the volume of pore space in a sample. It would be very hard to estimate the degree of this effect, but the Long Valley soils, due to their loose or unconsolidated state, are probably not significantly affected.

Soil Moisture. Errors associated with the determination of water in the soil samples could come from several sources. The Long Valley samples were considered to contain fairly fresh (pure) water so that using a specific gravity of 1.0 to determine a volume of moisture from weights of moisture would introduce a neglibible amount of error. Errors could arise in the drying of a sample during the determination of the amount of water present. If a sample were incompletely dried, the recorded amount of water would be less than the actual amount. For the average soil moisture of 0.82 cc errors associated with drying were assumed to be no greater than +/-0.25 cc. This introduces an average calculated variation in the mean helium in pore space concentration of +/-0.1 ppb. An increase of 0.25 cc, for a total of 1.07 cc water, would give a helium in pore space concentration of 5392.2 ppb, and a decrease of 0.25 (0.57 cc total) would give 5392.1 ppb.

Another possible source of error in the measurement of soil moisture could occur if a significant amount of water vapor present in the sample was removed during the determination of gaseous pore space. Evacuation of a sample during the pore space determination could draw off water vapor in a sample container, along with air. A brief experiment was done to examine how much water vapor is actually drawn off during the 30 seconds of evacuation with a vacuum pump. A series of 20 ml Vacutainers were filled with about 15.0 g of distilled water and allowed to equilibrate to room conditions. It was found that after 30 seconds on the vacuum pump an average weight loss of 0.007 g was observed. If this can be considered close to an upper limit on the amount of water that can be lost from a typical soil sample during evacuation, it can be used to examine possible error introduced by this procedure. The Long Valley samples had an average value of 0.82 g or 0.82 cc of soil moisture. A loss of 0.007 g of water would represent a loss of 0.8%. This would result in an increase to the measured amount of water that existed in a sample. Taking the average amount of water, converting to volumes, and adding what might be lost (0.82 cc + 0.007 cc) yields a total of 0.827 cc. Using this larger value of water in the calculation of helium in pore space does not significantly alter the helium in pore space concentration of 5392 ppb. This suggests that even though the amount of water that is being removed during the evacuation procedure may be a seemingly significant amount of the total soil moisture, it does not create a significant amount of error in the calculated value of helium in pore space for the Long Valley samples.

<u>Headspace.</u> Errors associated with the determination of the amount of headspace in a soil sample would be created in the method used to make the headspace measurement. The method includes measuring the height from the top of the soil to the top of the rubber stopper, assuming an average volume for the indentation within the rubber

stopper, and using an average diameter for a 20 ml Vacutainer. Errors in the determination of the volume of headspace could arise from the incorrect measurement of the airspace height due to the presence of small stones or debris on the top of the sample which would create an uneven surface from which to measure the height. If this error in measurement resulted in headspace determinations that were only correct to +/-1.0 cc, this would create an error in the mean calculated helium in pore space concentration of +/-12.0 ppb. A gain of 1.0 cc to the average headspace volume of 5.9 cc would yield a helium in pore space concentration of 5380 ppb, and a loss of 1.0 cc would yield a concentration of 5410 ppb.

From a series of measurements it was determined that an average volume for the stopper's internal indentation was 0.37 cc. Variations among stoppers was found to be no greater than +/-0.15 cc. Introducing this variation into the calculation of helium in pore space gives a concentration that differs from the average of 5392 ppb by +/-2.0 ppb.

Very little variation in the diameters of the 20 ml Vacutainers was found, thus error resulting from using a standard diameter of 1.4 cm would be negiligible.

Laboratory Temperature. A sample or laboratory temperature, T_1, of 30^{o}C was used for the Long Valley samples, since this was the temperature of the oven they were removed from prior to analysis. Error in the assumed sample temperature could be created if the samples cooled before the analysis occurred. Since only a short period of time elapsed between removal and analysis, the amount of cooling should not exceed 1.0^{o}C. A drop of one degree centigrade yields a helium in pore space concentration that does not differ significantly from the mean concentration of 5392 ppb. This indicates that a drop in temperature of this amount would not introduce any significant error in the calculation of helium in pore space concentrations.

Container Pressure. For the Long Valley samples the actual pressure existing in the sample container prior to analysis was not directly measured. An approximation of this value was made by calculating what the pressure would be due to thermodynamic changes within the container. The use of this value as an indication of the pressure within the sample container is dependent on the assumption that there is no gas production or loss within the Vacutainer, between the time of collection and analysis. The oxidation of metals such as iron in soils by water, would produce hydrogen gas which could increase the measured pressure within the container. Oxidation by oxygen gas would use up contained oxygen resulting in a possible reduction in the container pressure. If there is organic matter in a soil sample bacterial action could produce methane or carbon dioxide which would increase the pressure inside the container. Leakage of gases (such as helium) out of the Vacutainer would also affect the pressure. The degree to which any of these processes occurs is hard to predict, but errors associated with a range of pressure changes were examined. A variation of +/-.001 atmospheres from a mean value of 0.80 atm would result in a change of +/-12 pbb from the 5392 ppb value. A larger variation of +/-.005 atm would result in helium in pore space concentrations that differ from 5392 ppb by +/-62 ppb. A much larger variation of 0.01 atm would produce a much larger range in error of +/-123 ppb. While these larger variations would have a more profound effect on the calculated helium in pore space values, gas production or loss may not occur to such a large extent except with unusual samples. For the Long Valley samples, variations in the calculated container pressures were assumed to be less than +/-0.001 atm for most of the samples. The calculated helium concentrations are a direct function of the pressure inside the sample container.

Henry's Law Constants. The Henry's law constants that appear in equation (93) are dependent on temperature. Constants for the average soil temperature at the time of collection of $16^{o}C$ would equal 1.4163×10^5 mol H_2O atm He/ mol He, and a laboratory temperature of $30^{o}C$ would equal 1.4587×10^5. This temperature difference of $14^{o}C$, corresponds to a difference of approximately 0.4×10^5 (above units) in the Henry's Law constant. Varying the Henry's Law constant for either the laboratory or field conditions by 0.04×10^5 yields calculated concentrations of helium in pore space that differ from the mean concentration of 5392 ppb by about +/-.2 ppb. The above results show that a large error in the temperatures used to determine a constant, result in little change in the concentration calculated for the helium in pore space.

Headspace Concentrations. Possible errors associated with the measured helium in headspace concentrations would also affect confidence in the calculated helium in pore space values. Errors generated through instrument variations and in the reading of the strip chart record are in the range of +/-20 ppb (depending on the senstivity of the instrument). Changing the helium in headspace concentration of 5322 ppb by +/-20 ppb in the calculation shows a corresponding variation from in the mean calculated helium in pore space concentration of +/-36 ppb. The helium in pore space value has a direct relation to variations in the measured helium in headspace concentration . The above results point out that obtaining a precise measurement of the helium in headspace concentrations is very important.

Total Error Estimate. The square root of the sum of the squares of the above error estimates would give confidence limits to the mean helium in gaseous pore space concentration--5392 ppb--of +/-40.3 ppb.

It should be noted that most of the calculated helium in pore space concentrations would have a much smaller range in error than the above estimate, which generally represents a maximum of variations. As with the previous section, the above analysis identifies the parameters appearing in the calculation of original helium concentrations that must be accurately measured. These would include the volume of headspace within a sample container, the volume of gaseous pore space within a soil sample, and helium in headspace concentrations.

DISCUSSION

In the previous section, it was estimated that a typical calculated helium in pore space concentration for the Long Valley survey had an associated error of +/- 40.3 ppb. This is a relatively small degree of error considering the range of values (-400 to 2500 ppb), and suggests that interpretations of these data can be done with a high level of confidence.

A regression analysis of helium in headspace versus calculated helium in pore space concentrations was done to examine possible relationships between the two on a point-to-point basis. A trend towards linearity was indicated in the cross plot so a lineear regression analysis of the data was done. The plot of the data and the corresponding line are presented in figure 15. Results of the regression are:

Equation of the line: $Y = (3.25901)X - 11855.7$

Coefficient of determination, $R^2 = 0.8929$

Coefficient of correlation, $R = 0.9449$

Standard error of estimate = 129.86

The high coefficient of correlation (0.945) suggests that for most

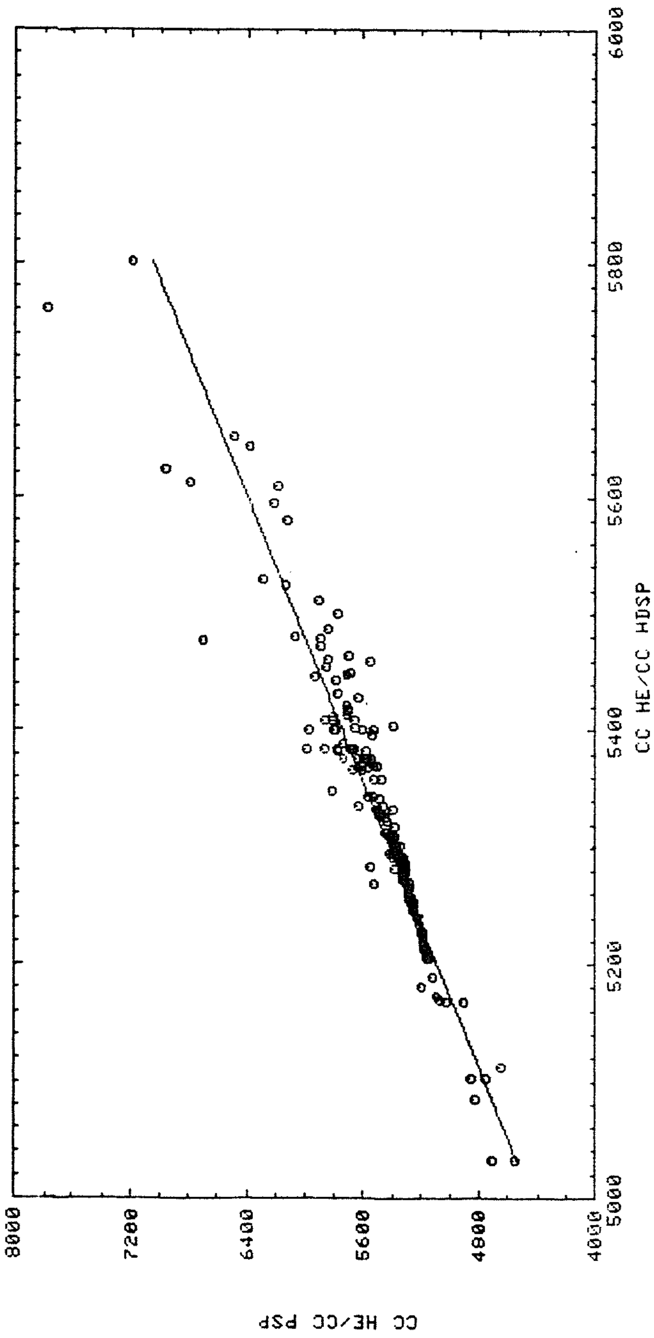

Figure 15. Linear regression analysis of helium in headspace versus helium in pore space concentrations, Long Valley.

of the samples calculation of actual helium in pore space concentrations has made no more than a relative difference from the helium in headspace concentrations. There are, however, some samples for which the application of the algorithm does seem to have made a significant difference.

Many of the samples that fall above the determined line in figure 15 are ones to which 10 cc of air had to be added to overpressurize them. A majority of the samples required the addition of only 5 cc to create a rebound and allow removal of a gas sample for analysis. This would indicate that consumption of gases occurred in the former samples. If container pressures inside these samples had been actually measured and used in the calculation of helium in pore space concentrations, the equation would correct for this consumption (or production) of gas.

A comparison of the smoothed Long Valley contour maps for helium in headspace data (figure 12) and helium in pore space data (figure 14) can be made. The anomaly pattern of helium in soils measured in the headspace without any corrections (figure 12) shows only small differences from the anomaly pattern of the calculated helium concentration in the soil pore spaces (figure 14). Both contour maps show a few areas of higher helium values, amid a discernable pattern of lower concentrations.

Examination of the two maps shows that the helium in pore space has smoother contour lines as opposed to the more ragged contours on helium in headspace. This may be due to the selection of contour intervals. This may also indicate that doing the corrections and calculations has reduced one of the significant sources of noise in the helium in headspace map - namely that the concentrations of helium obtained from headspace analyses are not as representative of actual concentrations as are the calculated concentrations.

From an exploration point of view, it would appear that for the study of soils in Long Valley, good results, as indicated by contoured anomaly maps, can be obtained by using the relative values of helium in headspace only.

Before inferences are drawn from this survey and applied to other helium in soil surveys, a few additional considerations should be made. If, instead of grid-like sample coverage (as in Long Valley) only sparse coverage or even traverse samples are obtained in an area, doing the determinations of actual soil concentrations may become very important on a point-to-point basis, since there may be less statistical averaging of noise.

The Long Valley samples that were collected were very homogenous. Soil types were similar and most were relatively dry and loose (unconsolidated). This homogeneity may result in the corrections having seemingly less effect than might be produced in surveys where dissimilar samples occur.

Many of the measured parameters, such as soil temperature and moisture, were found to be very constant in the Long Valley study, showing only small amounts of variation. The calculation of helium in pore space may become critical to the correct interpretation of a survey if these parameters do vary considerably, and especially if large regional differences are exhibited.

Thus, there may be several instances where doing the additional measurements to calculate a helium in pore space value rather than relying on helium in headspace values could yield greater confidence in the interpretation.

PART II

FIJI ISLANDS, SOUTH PACIFIC

The Fiji Islands are located in the Southwest Pacific, approximately 1600 km north of New Zealand, as shown in figure 16. Interest in the petroleum potential of this area has been encouraged by discoveries of oil and gas in Indonesia, Java, New Guinea, Malaysi, the Philippines, New Zealand, and more recently Tonga. Options on oil exploration licenses (OEL), covering onshore and offshore average in Fiji, were obtained by Pacific Energy and Minerals, Ltd., Colorado Springs, in 1978. In 1980, Pacific Energy and Minerals entered into a farm out agreement with U.S. and Canadian independents to conduct an exploration program, including exploratory drilling, on OEL 7 and 9 figure 17. This group was led by Bennett Petroleum Corp., Denver. Onshore and offshore exploration efforts were largely directed towards OEL 7, which lies on the east side of Fiji's largest island--Viti Levu.

Fiji is part of an island arc-trench volcanic system. The petroleum potential of such areas is not well understood, and consequently there has been little exploration of the basins in island arcs, except in Indonesia and perhaps the Philippines. The search for petroleum deposits in Fiji was initiated after the discovery of oil seeps in Tonga. Geological and geophysical studies were then conducted to examine such factors as proper thermal history, effective migration, adequate reservoirs, and sufficient traps in Fiji.

Geologic mapping of Fiji, while limited by the rough terrain, has shown that most of the rocks are Tertiary in age. Radiometric age dating and fossils indicate that the oldest known rocks of Viti Levu

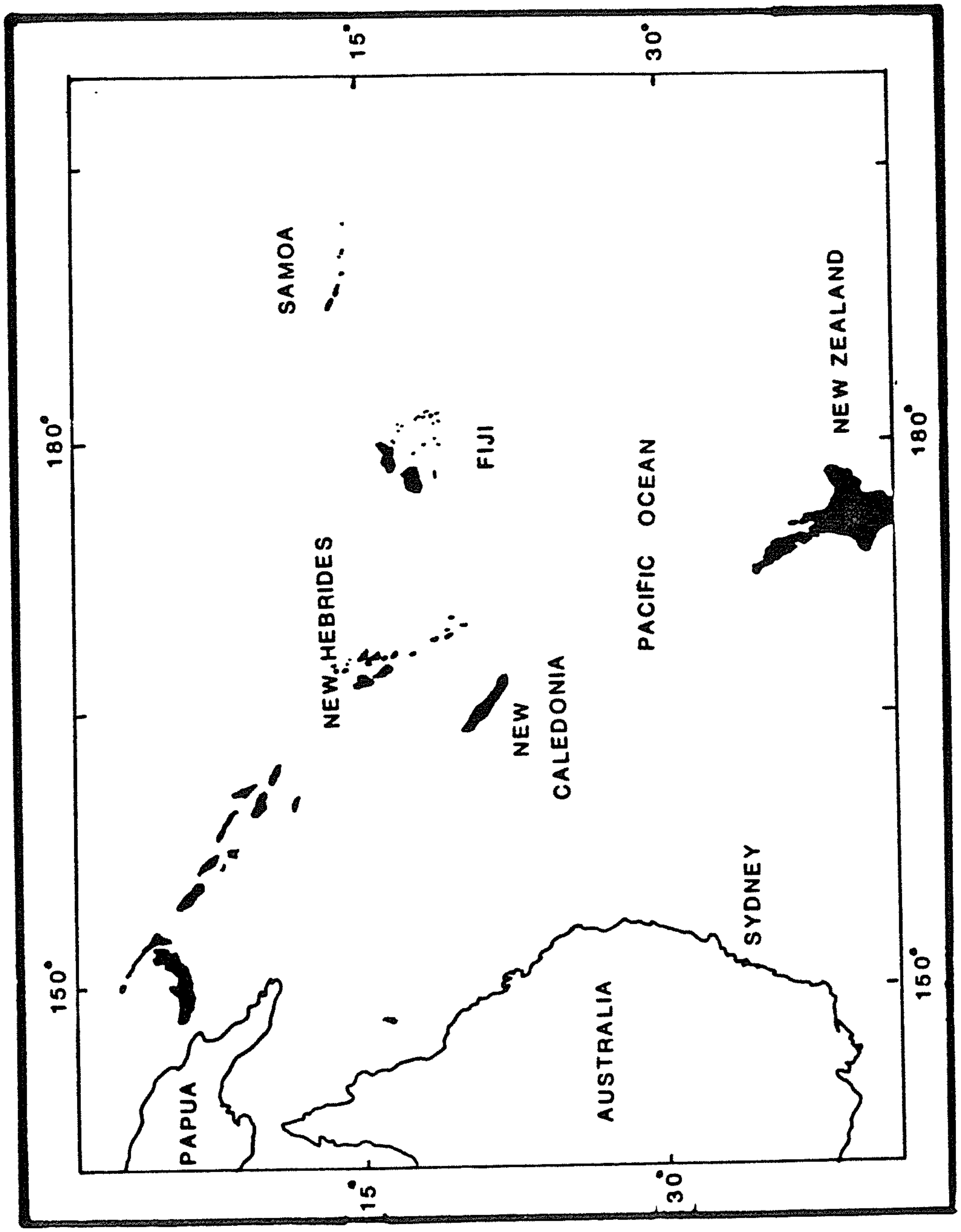

Figure 16. Geographic location of the Fiji Islands.

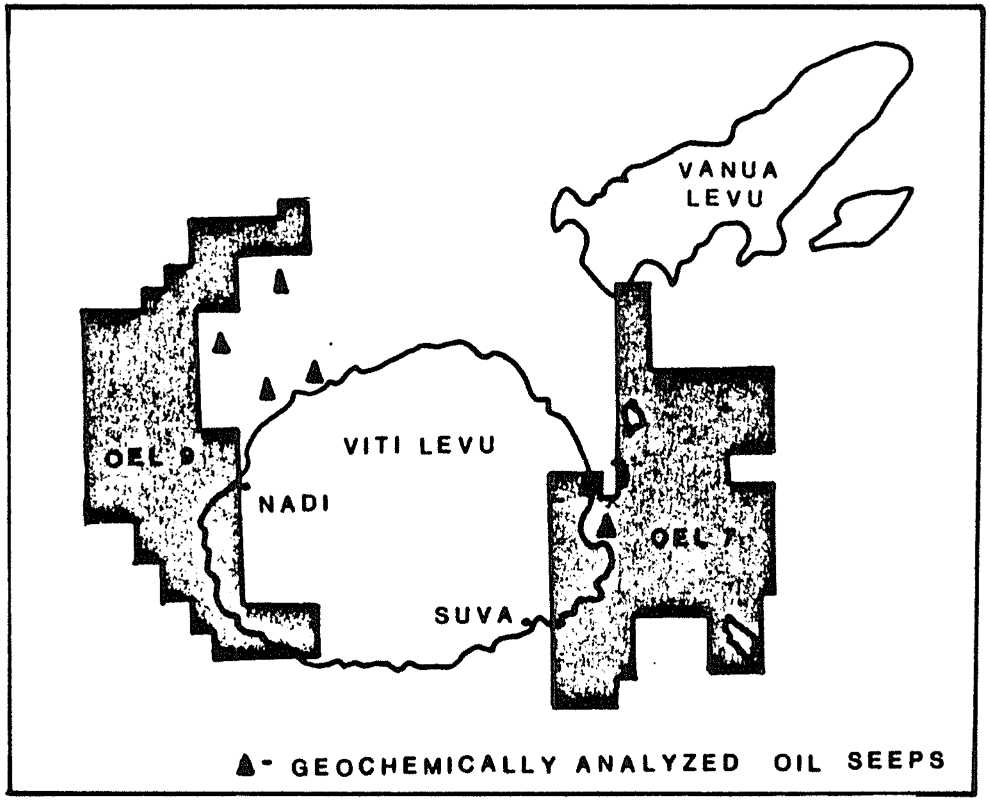

Figure 17. Locations of Oil Exploration Licenses and geochemically analyzed oil seeps, Fiji.

are Upper Eocene to Lower Oligocene. These rocks consist of andesitic volcanics and limestones. Younger units consist of sandstone, mudstone, limestone, volcanic rocks of andesitic and basaltic composition, and intrusive plutons, stocks and dikes of varying composition (Rodda, 1967).

Since Miocene reefs provide productive reservoirs and traps in many Southeast Asia oil and gas fields, similar reef structures were looked for in Fiji. Onshore field work in Fiji revealed a laterally extensive and thick section of Miocene limestone reefs, with a trend that appears to extend offshore. Additionally, outcrops of cavernous Eocene limestone were found, which may represent an additional reservoir target. Offshore seismic investigations indicate the presence of what are believed to be reefal anomalies possibly of Miocene age and anticlinal formations believed to be high porosity Eocene limestone.

In Fiji, several oil and gas condensate seeps have been identified at offshore and onshore localities (figure 17). Geochemical analyses of sediments around an active offshore seep indicated that the hydrocarbon content and the compound distribution pattern from extracted sediment were typical of mature petroleum.

There is thought to be an extensive Eocene to Recent marine sedimentary section, some 25,000 feet in thickness, in the Fiji area (Stoen, 1979). Volcanically derived marine shales within this sequence may contain sufficient amounts of organic carbon to provide possible source rocks for petroleum. In addition to being possible reservoirs, the reefal complexes or Eocene limestones could contain sufficient organic matter to be considered possible source rocks. Evidence of high subsidence rates coupled with a large geothermal gradient in the Fiji area suggest that there may have been a sufficient thermal history to generate hydrocarbons, despite the young age of possible source rocks. Non-porous and impermeable volcaniclastic rocks present in the Fiji area could serve as cap or sealing rocks to potential reservoirs.

Previous drilling in Fiji was done by Chevron Overseas Inc. and MAPCO Fiji, Inc., in 1980. Two offshore wells were drilled north of Viti Levu. While both yielded valuable information on structural and stratigraphic trends, the holes were dry.

An active exploration program was planned and conducted by Pacific Energy and Minerals beginning in August 1981. The program included seismic work, gravity and magnetics surveys, hydrocarbon geochemical surveys, exploratory drilling, and the helium geochemical survey described here.

Fiji is ideally suited to the use of unconventional exploration techniques due to the limited availability of geologic data. Further, the South Pacific offers an area free of any previous petroleum development and an environment different from those of previously conducted helium surveys. The Fiji helium survey was initially performed to study the feasibility of such a survey in this area, possible applications to interpretation of other exploration data, and possible use in the selection of onshore drilling sites.

The development in the Long Valley helium survey of equations for calculating the concentrations of helium in soil samples provides an additional means of evaluating the helium survey in Fiji. As described in the section on Calculation of Helium Concentrations there are several parameters that need to be determined in order to calculate the concentration of helium in a soil sample. At the time of the Fiji survey, many of these factors were not known, and consequently, measurements of volumes of soil pore space, volumes of headspace, field barometric pressures, and soil temperatures, were not taken.

It was decided to make assumptions of what the unmeasured parameters may have been, thereby allowing calculation of helium concentrations in the soil samples to be made. The reliability of data generated in this manner was evaluated by examining the Fiji survey assumptions in a manner similar to the error analysis done on the Long Valley data. Contour maps were generated for the raw data (helium in headspace concentrations) and for the corrected data (helium in soil porespace concentrations). A comparison of anomaly patterns between the two maps was made and inferences to petroleum potential for the area were drawn.

Climate and Soils in Fiji

Fiji has a humid, tropical climate. The daily (diurnal) and seasonal range of temperature in lowland Fiji is comparatively small.

The mean annual temperature averages 25^{o}C. The range of the monthly means of temperature variation in a year is between 6 and 8^{o} C. Annual rainfall for Viti Levu is between 250 and 500 cm (Twyford and Wright, 1965).

Soil types encountered in the survey included:

a. Recent soils from coastal sands or alluvium derived from deltaic river deposits.

b. Dark colored soils having a loamy composition.

c. Clayey soils often ferruginous and gravelly.

d. Swampy soils including gleys and marine marsh muds.

While no regular soil temperatures measurements have been made for Fiji, those of the humid tropics often range between 21^{o}C and 32^{o}C, with a mean in the vicinity of 29^{o}C (Twyford and Wright, 1965). Soil conditions are almost continuously moist.

METHODS

The following section presents the methods used for sample collection and analysis of the Fiji samples. Additionally, treatment of the resulting headspace data is discussed, including correction for the dilution created by adding air to the sample container prior to analysis, and the approximations and assumptions made to allow the calculation of helium in soil concentrations.

Sample Collection

A total of 213 soil samples were collected over the onshore area of Oil Exploration License 7, on the east side of Viti Levu (fig. 17). Sampling sites were located along the eastern coastline and alongside existing roads. Samples were collected approximately 0.5-1.0 km apart. In general, grid-like coverage was obtained. Sample locations are shown in the Results section and tables of sample numbers, latitudes, and longitudes are presented in Appendix C.

The low cost and ease in handling and shipping of Vacutainers encouraged their use for helium in soil-gas surveys by the private contractors. Vacutainers were chosen for use as soil-gas sample containers for the Fiji survey. When soil conditions in Fiji prevented the collection of soil-gas samples, Vacutainers were used for the collection of actual soil samples, although very little work had been previously done using or evaluating this type of sample container for the collection of soil samples.

Before sample collection, the Vacutainers were uncapped and allowed to equilibrate with atmospheric air in order to remove any residual helium. When sampling along roads, sample sites were located about 5-10 meters off the roadside in undisturbed (unplowed, etc.) areas. Samples were collected by digging a hole about 45 cm deep and placing soil from the bottom of the hole into a specimen tube. The Vacutainers were filled about three-quarters full. When possible, care was taken to avoid the inclusion of small stones and organic debris. Dirt was wiped away from the inside of the tube neck, and the rubber stopper replaced. At the end of each day, the Vacutainers were sealed with silicone sealant to inhibit leakage of gases from around the seal.

General soil types, time of day, precipitation events, obvious differences in vegetation, and air temperature were recorded for most of the samples. Sampling was conducted concurrently with a gravity and magnetics survey. During early stages of the survey, samples were collected along the eastern coastline. These soils were often composed of marine marsh muds. Later in the survey, inland samples were collected which often were composed of deltaic alluvium and clayey soils. Collection of samples was done from late September through late December, 1981.

Sample Analysis

Samples were shipped back to the United States in styrofoam sleeves, and analyzed commercially by Hager Laboratories in Denver.

Samples were received by Hager Laboratory three to six weeks after collection. Soil samples were agitated in an ultrasonic bath for 30 minutes, then stored three to five days before analysis. This was done to allow helium in the pore spaces of a soil to equilibrate with helium in the headspace of the container. Three cc's of laboratory air were mixed with headspace gas in each soil, after which 3 cc's of headspace gas were removed for helium analysis. Air was added to the sample containers in order to overpressurize the sample, thus allowing the withdrawal of a gas sample. The dilution that is caused by the addition of air was not corrected for in the reported helium in headspace values, but is corrected for in the following section on Data Treatment.

The resultant gas samples were analyzed using a modified CEC helium mass spectrometer. The three cc's of sample withdrawn from the pressurized Vacutainer were injected into a constant pressure inlet system. The injected sample was metered into the mass spectrometer through a liquid nitrogen chilled charcoal trap.

An air standard was measured after each sample. The difference between each pair of air samples was recorded and a standard deviation between a series of about 30 pairs was calculated. The standard deviation between pairs of air standards run for the Fiji samples ranged from 30-70 ppb. Hager Laboratories reported that this standard deviation should be considered as a system noise level. A high reference gas containing 5420 ppb of helium was periodically analyzed.

Helium concentrations were reported as parts per billion above or below an air standard of 5240 ppb.

After analysis, the soil samples were weighed, dried and reweighed, and a soil moisture content was calculated.

Data Treatment

Few of the soil samples collected in Fiji contained standing water in them, and it is likely that the majority of these soils contained significant amounts of gaseous pore space. This was supported by the measurement of pore space in soils collected at a later period. Therefore, it was decided to use equation (93), which calculates the concentration of helium in gaseous pore space, the estimated or measured parameters (discussed below), and the reported helium in headspace values corrected for dilution, to estimate actual concentrations of helium that existed in the soil samples.

Dilution by Overpressurizing. Three cc's of laboratory air was added to the sealed Fiji samples prior to analysis. As with the Long Valley survey, the dilution that this creates must be corrected for before a determination of the actual helium concentration existing in the sample can be made.

As presented in Part I, the concentration of helium that existed in the headspace of the sample container prior to dilution with air can be found from:

$$[He]_{corr} = \frac{[He]_{meas} \cdot (V_h + V_a) - 5240\ V_a}{V_h} \quad (103)$$

where

5240 = the concentration of helium in air, ppb

V_h = the amount of gaseous headspace in the sample container, cc's

V_a = the amount of air added to overpressurize the sample container, cc's

$[He]_{meas}$ = the absolute concentration of helium measured in the sample container, ppb

$[He]_{corr}$ = the concentration of helium in the headspace corrected for dilution, ppb

The above equation assumes that complete (100%) equilibration occurs between the added air and the gaseous headspace. Since equilibration between these two should occur rapidly, this is probably a valid assumption for the Fiji samples. This equation also assumes that no equilibration between the added air and the gaseous soil pore space occurs. The extent to which equilibration between the injected air and the soil pore space occurs during the time prior to analysis depends on the soil type.

In a sandy soil, the movement of air and water is fairly rapid due to the dominance of larger soil interstices. In heavier soils gas and water adjustment is slower due to the dominance of smaller (micro) intertices. This is despite the fact that heavy soils contain larger amounts of pore space (greater porosity) than sandy soils (Lyon and Buckman, 1943).

For the Long Valley survey where soils were dry, loose, and fairly sandy, and samples were stirred using a Vortex stirrer after the addition of air, the assumption was made that the added air had undergone complete equilibration with the headspace gas and the gaseous soil pore space. Therefore, the calculation of helium concentrations prior to dilution was made using:

$$[he]_{corr} = \frac{[He]_{meas}\,(V_h + V_a + V_p) - 5240\,V_a}{V_h + V_p} \qquad (104)$$

where

V_p = the amount of gaseous pore space in a sample, in cc's

For the Fiji survey, soil samples were differentiated by four approximate soil types. Clayey samples represented about 58% of the total number of samples collected. Highly sandy samples represented 12% and when possible were generally avoided during collection. Loamy samples were found to comprise about 19% of the samples, and marine or marsh (mangrove swamps) about 11%. Equation (104) was used to correct for the incurred dilution for those samples which were classified as sands or largely sand, and equation (103) was used to treat the other soils that were collected, and were largely composed of clays.

Neither of the above equations would yield an accurate concentration of helium prior to dilution if any equilibration between soil pore space of heavier, or clayey, soils and the air added prior to analysis occurred, or less than 100% equilibration between the sandy samples and the added air occurred. This would result in error being introduced in the calculation of helium in pore space concentration. This is considered in the section on Evaluation of Parameter Errors, Fiji.

Appendix C contains tables of the samples, soil types, calculated pore space volumes, measured helium in headspace concentrations, helium in headspace concentrations corrected for dilution, and the difference between the two concentrations.

Approximations of Temperature and Pressure. Unlike the Long Valley helium survey, soil samples collected in Fiji were not equilibrated in a constant temperature oven before analysis. Therefore, an accurate measurement of the temperature of the samples at the time of analysis is not available. However, since laboratory temperatures do not greatly affect the calculation of helium in the gaseous pore spaces of a soil, the assumption was made that the samples were at a typical room temperature of 22°C prior to analysis.

Soil temperatures were not measured during the Fiji survey, but for many of the sample locations air tempertures were recorded. Measured air temperatures ranged from 25-36°C. It has been suggested that soil temperatures in Fiji may fall within a similar range to the recorded air temperatures (Twyford and Wright, 1965). Therefore, the assumption was made that air temperatures are, for the most part, very similar to soil temperatures at the depth of sampling. Thus, in the calculation of helium concentrations in the soil samples collected in

Fiji, measured air temperatures were used in place of soil temperatures. Since variations in the soil temperature do not have a large effect on the calculation of helium in soil pore space, the use of air temperatures instead of soil temperatures should not introduce a singificant amount of error. For samples for which air temperatures were not taken, the mean of the measured air temperatures--30°C--was used.

Barometric pressures at sampling locations were not measured for the Fiji survey. It is likely that variations in pressure do not have a large effect on the calculation of helium concentrations in soil pore space. Additionally, elevation changes within the survey were small. A large majority of the samples were collected within 15 m of sealevel. The maximum elevation difference encountered within the survey was 90 m. Therefore, instead of field barometric pressures, pressure data from weather records was used in the calculation of helium in pore space concentrations.

Daily pressure data for the period of the survey were not available, but monthly data from previous years were available from published World Weather Records. The weather station for Fiji is situated at Lauthala Bay in Suva. This is within the area of the helium survey. Observations were taken at 5.5 m above sealevel. Average monthly pressures at sea level were reported as means of 24 hour periods. Monthly pressure means over ten year periods were also given (World Weather Records, 1959).

For the Fiji survey, average pressures for the months of sample collection (September, October, November, and December) were used. Pressure values were estimated by taking the monthly means of reported pressures during the period of 1941-1970. For samples collected during the month of September, a barometric field pressure of 1.0008 atm was assumed. For October, a pressure of 1.0001 atm was used; 0.9977 atm for November; and a pressure of 0.9956 atm for samples collected during December.

Approximations of sample headspace and porespace volumes. While soil sample containers used in Fiji were filled to a similar level, the actual amount of headspace existing within the sample container was not measured. Neither was the amount of gaseous soil pore space measured. Using an assumed volume of headspace for each sample, a volume of gaseous pore space was calculated as described below. The assumptions made and their resultant effect on the calculation of helium in pore space concentrations are examined in the section on Evaluation of Parameter Errors, Fiji.

If the volume of the soil sample before and after drying can be measured or estimated and the volume of water in a sample is known, an approximate volume of gaseous pore space in a sample can be calculated as follows. The total volume of an undried soil sample is composed of the soil particle volume, and the volume of the soil pore space (the pore space of a soil being occupied by air and water in varying proportions). Thus:

$$V_s = V_d + V_w + V_p \qquad (105)$$

where

V_s = the total volume of an undried soil sample

V_d = the volume of the soil particles, or dry soil volume

V_w = the volume of water in a soil

V_p = the volume of air in a soil, or gaseous pore space

If an assumption is made as to the volume of headspace within a contained soil sample, the volume that the soil itself must occupy can be found by substracting the headspace volume from the volume of the sample container:

$$V_s = V_c - V_h \qquad (106)$$

where

V_c = the volume of the sample container

V_h = the volume of headspace in a sample

Estimating the volume of the soil before drying (equation (106)) and measuring the volume of water in a soil leaves two unknown variables in equation (105)--the volume of the dry soil, and the parameter of interest--the volume of gaseous pore space.

Using the weight of soil obtained after drying, an approximate volume of the dry soil can be found. The weight of the soil particles themselves can be found from their specific gravity. Specific gravity is unaffected by soil condition and remains the same whether the soil is loose or compact. The values for purely mineral soils usually vary within a narrow limit of 2.6 to 2.7 (Lyon and Buckman, 1943). Organic matter, if present in significant quantities, is the only common constituent of soils that can cause the specific gravity of a soil to deviate from this range. For general calculations, the average near-surface soil may be considered as having a specific gravity of about 2.65. Therefore, the volume of the dry soil (soil particles) can be found by:

$$V_d = \frac{M_d}{2.65} \qquad (107)$$

where

M_d = the weight of the soil after drying

The substitution of equation (107) into equation (105) and rearrangement yields an expression for finding the volume of gaseous pore space in a soil:

$$V_p = V_s - (V_w + \frac{M_d}{2.65}) \qquad (108)$$

For the Fiji survey, efforts were made to collect similar volumes of soil for each sample. It was determined by experiments with a variety of sample collection tubes that a typical volume of a 10 ml Vacutainer was 12.5 cc. For a nominal Vacutainer volume of 12.5 cc, filling the tube with soil to slightly less than three-fourths full would yield a volume for the headspace of 3.5 cc. This procedure also allowed an estimation of the volume of the undried soil sample to be made. Following equation (106), the difference between the volume of the sample container and the volume of the headspace would yield a soil volume of 9.0 cc.

The assumption was made that the measured weight of moisture in each sample had a density of 1.0 g/cc. Therefore, the weight of water was equivalent to the volume of water in a sample:

$$\frac{1.0\ g}{1.0\ g/cc} = 1.0\ cc\ H_2O \qquad (109)$$

Substitution of the total volume of the undried soil, 9.0 cc, and the weight (or volume) of soil moisture measured for each sample into equation (108) allowed a value to be obtained for the volume of gaseous pore space in a collected soil sample.

RESULTS

Several of the soil samples collected in Fiji exhibited only small amounts of calculated gaseous pore space volume. As with the Long Valley survey, a small pore space volume creates a large degree of error in the calculation of helium in pore space concentrations. Of the 213 soil samples collected in Fiji, 29 or 16% had pore space volumes of less than 1.0 cc. These samples were considered to have a high degree of uncertainty in their calculated helium concentrations and were not included in the examination or contouring of the helium in pore space data.

Concentrations of helium in the headspace of the Fiji soil samples, uncorrected, ranged from -400 to 1000 ppb helium in excess of helium in abient air. The mean and standard deviation is 386 +/-231 ppb He for the 213 samples. A frequency plot of the data is given in figure 18. The data exhibited roughly a normal distribution. Results are depicted as a smoothed contour map of helium concentrations shown in figure 19.

Concentrations of helium in gaseous pore space of soil samples calculated using equation (93) ranged from -640 to 4560 ppb He. The mean and standard deviation is 1733 +/-1048 ppb for 174 samples. Results exhibited skewness towards the high side, as shown by the frequency diagram figure 20. A smoothed contour map of the calculated helium concentrations is presented in figure 21. As with the Long Valley data, contouring of the data was done using a computer program

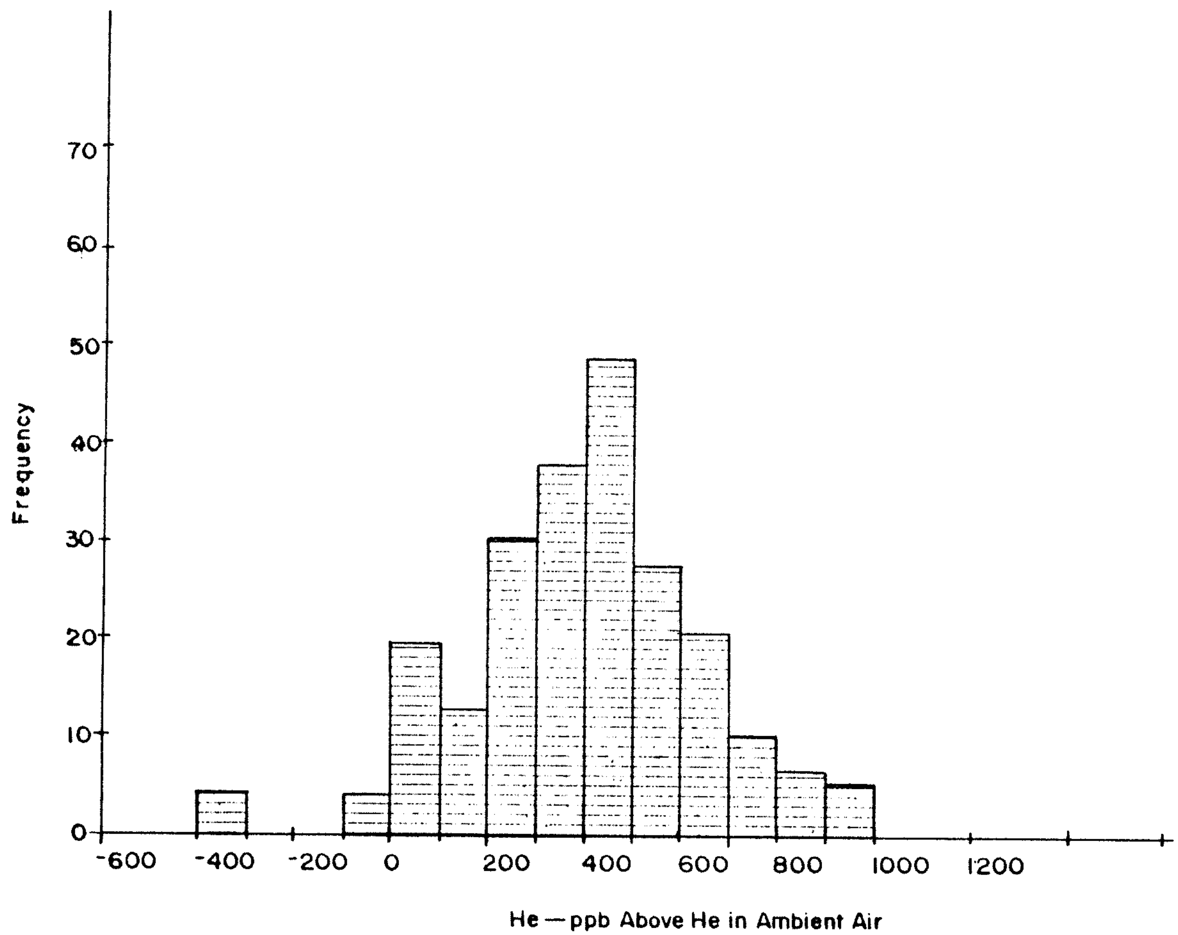

Figure 18. Frequency diagram of uncorrected helium in headspace concentrations, Fiji.

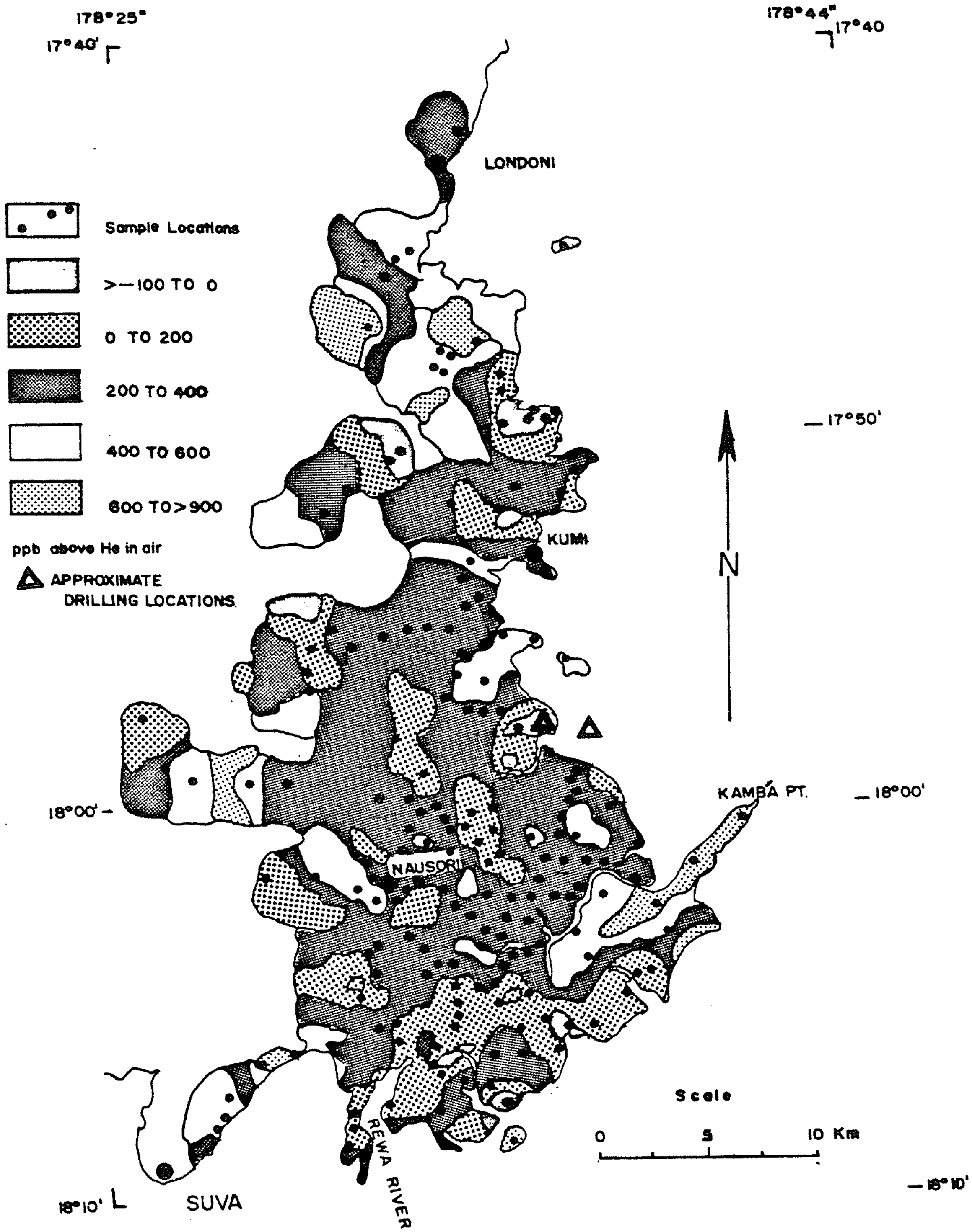

Figure 19. Smoothed contour map of uncorrected helium in headspace concentrations, Fiji.

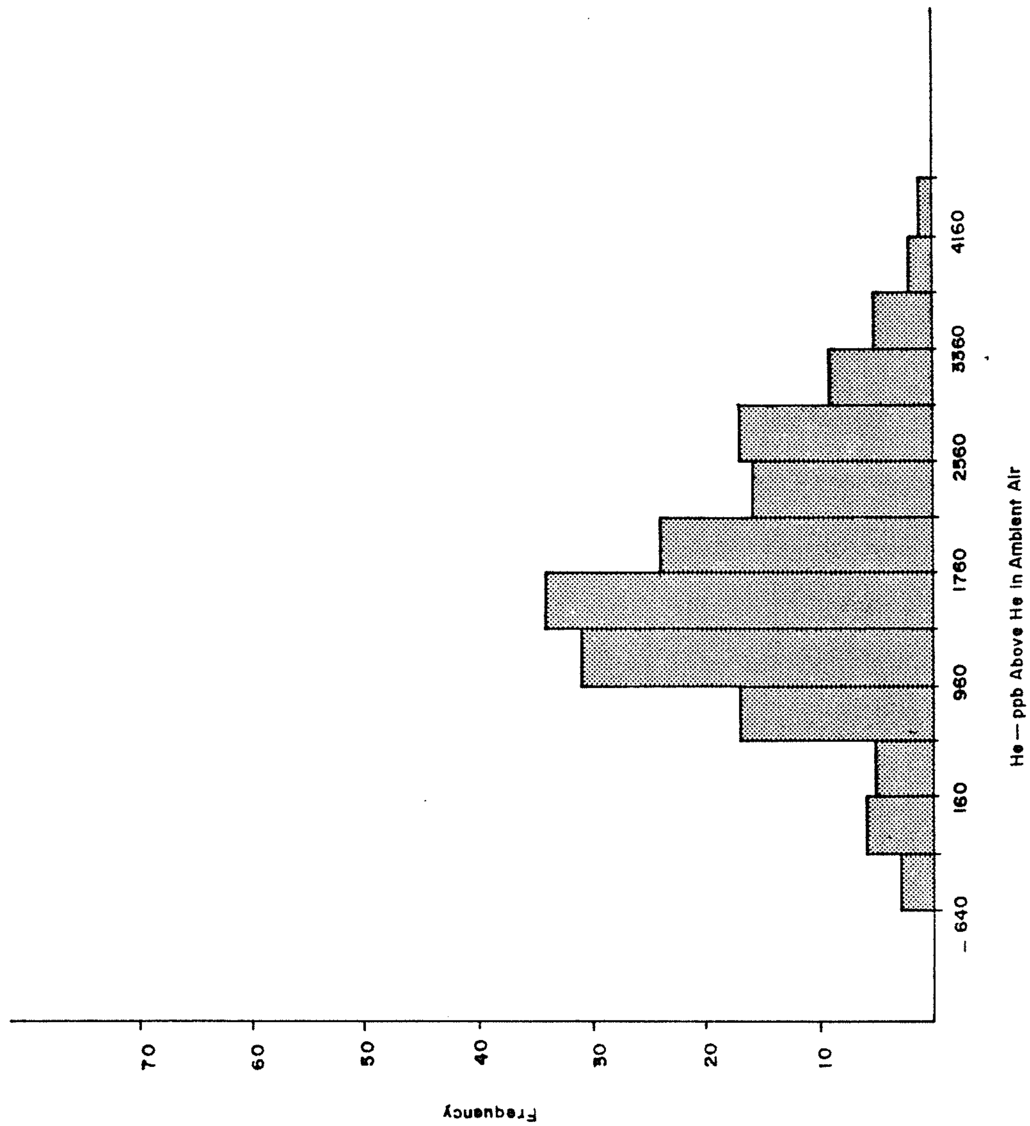

Figure 20. Frequency diagram of calcualted helium in gaseous porespace concentrations, Fiji.

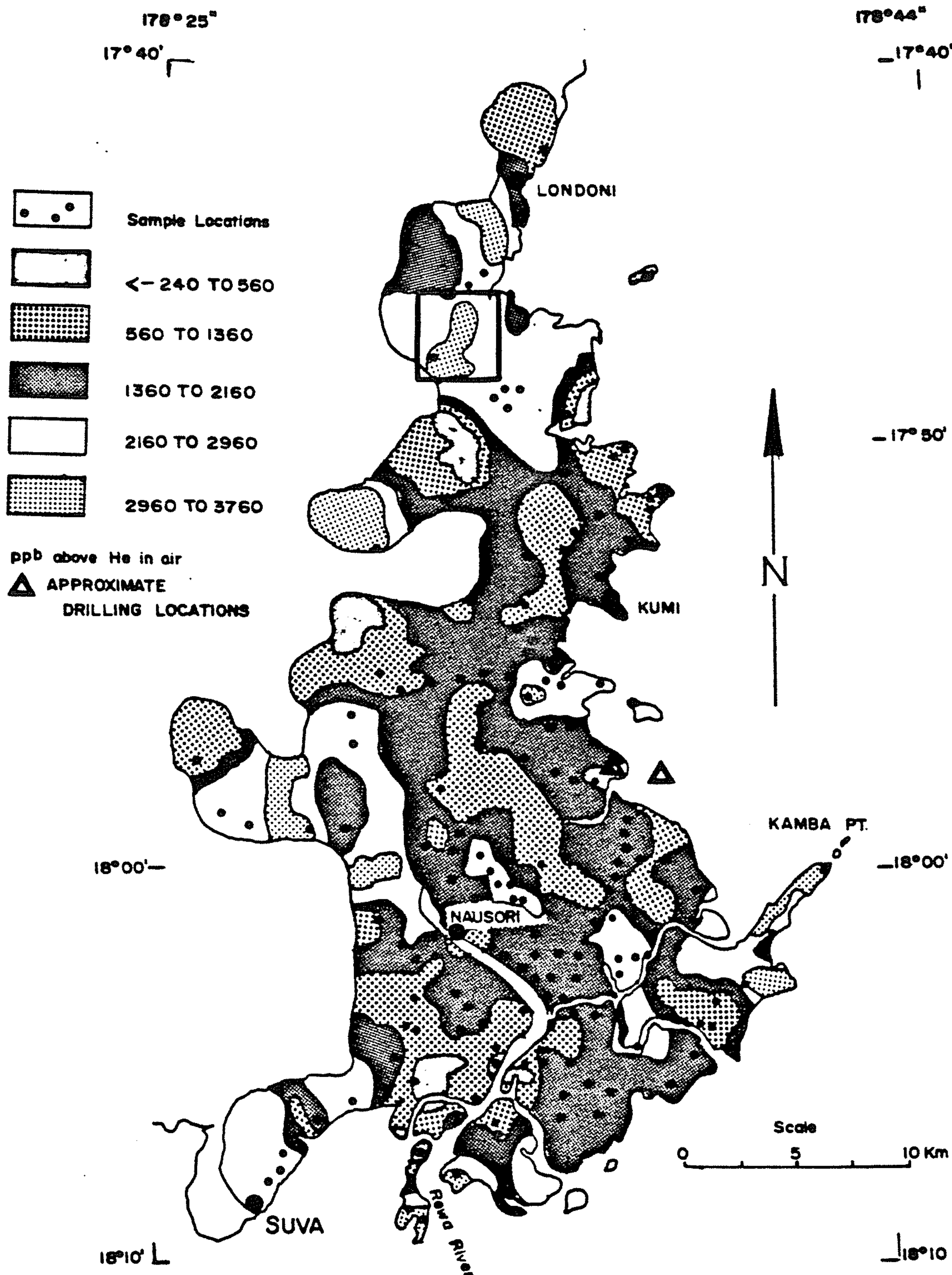

Figure 21. Smoothed contour map of calculated helium in gaseous pore space concentrations, Fiji.

written for the HP 9825A desktop computer (Reimer and Dean, 1979). This program allows for a smoothing of the data by the concentrations of nearest neighbors weighted inveresely by the square of the distance to the neighboring samples. For Fiji, an approximate search radius of 1.5 km was used, this would include four to five samples.

Appendix C contains tabulated data for the soil samples collected in Fiji, including sample locations, weights of wet and dry soils, amount of sample water, assumed or measured air temperture, calculated volumes of porespace, assumed atmospheric pressures, calculated field pressures, helium in the headspace concentrations helium in the headspace concentrations corrected for dilution, and calculated values for helium in pore space concentrations.

As was done with the Long Valley survey, an examination of the variation of parameters on the gaseous pore space concentrations was done and is presented in the following section. In this examination, estimations of the amount of error present in these results were made. It is important to examine the degree of such errors before conclusions are drawn from the Fiji data.

EVALUATION OF PARAMETER ERRORS, FIJI

It is necessary to examine the amount of error associated with the calculated helium in pore space concentrations to establish confidence limits for the data. This allows a determination of how valid the calculated values obtained are, in light of the many approximations that had to be made to treat the raw data. This was done in a manner similar to the Long Valley survey by estimating the amount of error related to individual parameters or variables that are involved in the calculation of a typical helium in pore space concentration.

Using equation (93) and the mean helium in headspace concentration for the Fiji samples of 5630 ppb, a resultant helium in pore space concentration of 6241 ppb was calculated. Then, an estimation of the amount of error associated with variables that appear in the calculation were made, and each parameter was allowed to vary by the amount of error. The new helium in pore space concentrations were then calculated, and the difference between the mean helium in pore space concentration (6241 ppb) and the concentration obtained by the variance was recorded. Finally, the resultant differences from the mean were combined to give an overall estimation of the error associated with the mean helium in pore space concentration. Results are presented in table 7 and discussed below.

Table 7. Differences from the mean calculated helium in porespace concentration (6241 ppb) caused by error estimates for the Fiji study.

Variable	Means of Variable	Error Estimate	Difference from mean (ppb)
T_f	30.6^{o}C	+/- 10^{o}C	+/- 4
P_f	0.998 atm	+/- .0052 atm	0
V_w	3.0 cc	+/- 0.25 cc	+/- 0.8
V_p	2.2 cc	+/- 1.43 cc	-239, +498
V_h	3.5 cc	+/- 1.0 cc	+/- 175
T_l	22^{o}C	+/- 2.0^{o}C	+/- 0.2
P_c	0.97 atm	+/- .003 atm	+/- 45
K_{He}	1.4514 x 10^{5}	+/- 0.315 x 10^{5} mol H_2O/mol He	+/- 14.7
[He] hdsp	5630 ppb	+/- 10 ppb	+/- 26
[He]corr. for dilution, clays	5953 ppb	+0.28 cc	-64
[He]corr. for dilution, sands	5884 ppb	-1.1 cc	+126

Total Error Estimate = +/- 549 ppb

Field Temperature. For the Fiji samples measured or average air temperatures were used instead of soil temperatures. No precise information is available on soil temperatures in Fiji, but some soil temperature readings were taken over a period of several hours during the Fiji survey. These are presented in table 8. These measurements show that soil temperatures are warm, fairly constant over five hour period, and only slightly lower than the air temperature measured in the morning. It can also be noted that temperatures remained fairly constant during and after a tropical rain. Generally, precipitation cools the soil, but since rains in Fiji are warm, there seems to be less of an effect. With these considerations, the soil temperature may be similar to air temperature under most climatic conditions. Many of the air temperatures used in the calculation of helium soil concentrations may vary from the actual soil temperatures by +/-5^{o} C. An even wider range in difference of +/-10^{o}C was used as an error estimate since so little data is available. This range in error is similar to the range of air temperatures measured during the Fiji survey (25-36^{o}C). Varying the mean air temperature of 30.6^{o} C by +/-10^{o}C yields a helium in pore space concentration of 6237 ppb with an increase of 10 degrees and a concentration of 6243 with a decrease of 10 degrees. The average difference from the mean helium in pore space value--6241 ppb--created by this variance would be less than +/-4 ppb. Thus, error in the calculation of helium in pore space concentration introduced by the use of air temperatures instead of soil temperatures

Table 8. Soil Temperatures in Fiji Taken at a Depth of Approximately 25 cm ver a Five Hour Period, November 1981. Air Temperature Equals 28^{o}C at 10:30 a.m.

Time	Soil Temperature, ^{o}C
9:00	27^{o}
10:00	28^{o}
11:00	27^{o}
12:00	26^{o} (Raining)
1:00	26^{o}
2:00	27o

is not significant for the Fiji survey.

Field Pressure. Again, pressure measurements were not taken in Fiji but examination of weather records shows a narrow range in barometric pressures in Fiji despite climatic and seasonal differences. As previously discussed, elevation changes within the survey were relatively small, and the period of sampling did not fall during the storm or hurricane season. Therefore, deviations in sampling site pressures from the mean monthly values that were used in the calculation of helium in soil concentrations were considered to be of managable magnitude. A maximal survey elevation change of 90 m (from sea level) would result in a pressure change of about 0.01 atm. The variation in reported monthly pressures for the period of the survey is 0.0052 atm.

Additionally, pressures would change with temperature. The estimated range in temperature for the Fiji samples, $25^{o}C-36^{o}C$, would result in a calculated change in the barometric pressure of about 0.04 atm. This is a large amount of variation in pressure but would represent a maximal change.

Summing these would give a variation in the pressure data of +/-.0552 atm. No information is available on the magnitude of barometric changes in Fiji due to passage of storm fronts, but such variation would add to the error estimate.

Using equation (93) and changing the field pressure value will not result in a difference in the calculated helium in pore space concentration. As with the Long Valley survey, this is proboably due to the use of calculated container pressures in the equation which may have a cancelling effect on field pressure variations.

Soil Moisture. An error estimate can be made on the measurement of soil moisture in each sample by considering errors in drying, and errors associated with using the specific gravity of pure water to calculate a volume of water from a weight of water. Errors in drying of the samples could result from incomplete drying which would give a reported weight of water that is less than the actual value. Errors resulting from obtaining a weight of soil moisture (weighing errors) are probably small. The weight of water obtained was converted to a volume of water by using the specific gravity of pure water--1.0 at $0^{o}C$. In the section on the Calculation of Helium Concentrations it was determined that the error generated by using a specific gravity of 1.0 at temperatures other than $0^{o}C$ are relatively small.

The error that may be introduced if soil moisture is not composed of pure water was not examined for the Long Valley survey, since soils were considered to contain fresh (pure) water. Possible leaching of salts in the soils could also cause deviations from purity. For many of the Fiji samples, the assumption that the soil moisture lacks salinity or other constituents which would alter its specific gravity from that of pure water is also probably valid. But several of the samples were collected at or near the coastline and for these samples the presence of marine water may alter the density of the soil moisture. If the moisture in these samples was entirely composed of normal marine water, the actual density would be about 1.0263 g/cc. Using the density of pure water (i.e. fresh) would introduce an error of +0.0263 cc for every gram of water in the sample. This is not a large amount of variation. Many of the coastal samples which might exhibit this deviation from purity also contained enough water to render the available amount of gaseous pore space unamenable to the calculation of pore space concentrations.

Consideration of the above factors suggests that an error estimate for the determined volume of water in the samples may be around +/-0.25 cc. Varying the mean moisture volume of 3.0 cc by this amount would give calculated helium in pore space values that differ from the mean by +/-0.8 ppb. This suggests that errors made in the measurement of soil moisture and errors resulting from the density of the moisture varying from 1.0 g/cc do not introduce a significant amount of error into the calculation of helium in pore space values. It should not be concluded at this point that deviations in soil moisture purity do not have any significant effect on the calculation of helium in pore space concentrations, since Henry's Law constants are also dependent on the constitution of the water.

Gaseous Pore Space. Since volumes of gaseous pore space and headspace used in the calculation of helium concentrations were not actually measured, it is important to examine possible errors associated with these parameters.

It is worthwhile to point out an alternative method for determining approximate volumes of gaseous pore space and why it was not used in the Fiji data treatment. Instead of assumptions on the volume of soil and the volume of headspace, assumptions on the percentage of porosity in a soil could have been made using its field classification as sandy or clayey. From this a volume of pore space and a volume of headspace could have been calculated as follows.

The porosity is that percentage of soil (by volume) that is filled with air and water, thus if an assumption is made as to the percentage of total porosity in a sample and the amount of water in the sample is known, a volume for the gaseous pore space can be determined. After the determination of the volume of the dry soil (using a specific gravity of 2.65), the volume of headspace can be found. The summation of the volumes of dry soil, soil moisture, and gaseous pore space would yield a volume for the total soil in the Vacutainer. Subtraction of the total soil volume from the volume of the empty Vacutainer (nominally 12.5 ml) would then yield a value for the volume of headspace in the sample. This would essentially be the reverse of the procedure used to establish approximate volumes for the Fiji samples (as discussed in Data Treatment).

The total pore spaces of a near-surface sandy soil vary within the range of 35-50%, while heavier soils vary from 40 to 60% (Lyon and Buckman, 1943). Surface sands and sandy loams usually contain somewhat less total pore space (or porosity) than silt loam, clay loam, and clays, due to the close contact of particles in sandy soils, while finer soils are generally lighter due to the tendency of the small particles to resist compaction. Since there is a wide range of possible porosities with soil type, it would be hard to establish an average porosity value for the Fiji soil types and samples. An approximation as to the amount of headspace in the samples collected in Fiji is better known than an approximate percentage of porosity (and hence the amount of gaseous pore space) since similar amounts of soil were collected. This would suggest that calculation of pore space volumes using estimated headspace, as was done with the Fiji data, would introduce less error into the results than estimating the amount of pore space and calculating the volume of headspace. Results from the Long Valley section of error analysis support this by showing that errors associated with the volumes of headspace create less error in the calculation of helium in soil concentrations than do errors associated with pore space volumes. Therefore, the calculation of the pore space volumes as opposed to the calculation of headspace volumes, is probably a more appropriate approach, and would introduce less error in the calculation of helium in pore space concentrations.

Returning to an examination of the error associated with the values determined for the volumes of gaseous pore space, the following equation was presented in the Methods section:

$$V_p = V_s - (V_w + \frac{M_d}{2.65}) \qquad (108)$$

where V_p is the parameter under consideration--the volume of gaseous pore space. An estimation of the errors associated withh individual variables appearing in the above equation allows an estimation of the error of the pore space determination to be made.

Beginning with V_s--the total volume of the soil sample (undried), Vacutainer tubes were for the most part filled with soil to a volume estimated to be 9.0 cc. A potential variation of +/-1.0 cc would indicate a range in the soil volumes of 8.0 to 10.0 cc. With the possible exception of marine marsh muds and extremely clayey samples, this may be a fair estimate of the actual range in soil volumes for the Fiji samples. Introducing a variation of +/-1.0 cc would also introduce a potential error of approximately +/-1.0 cc in the calculation of pore space volumes. This is an approximation since the amount of water and the weight of soil should also change with a variation in the volume of soil, but were held constant in the error analysis.

As previously examined, errors in the determined amount of water in each soil sample incurred through incomplete drying and using a specific gravity differing from that of pure water, might introduce errors that are on the order of +/-0.25 cc. This, in turn, would result in a possible error in the calculation of pore space volume by +/-0.25 cc.

Another possible error in the calculation of pore space volume could result if the specific gravity used for the dry soil differs from 2.65 g/cc. As discussed in the Long Valley analysis, error in using this value would probably be less than 0.1 g/cc. Introducing this range into the calculation of pore space volume yields a possible variation of +/-0.07 cc.

Finally, error in calculating the volume of pore space may arise if the weight of soil used is incorrect. This could result from improper weighing of the sample or from variations in Vacutainer weights (a nominal Vacutainer weight was subtracted from the total weight of the tube and soil to obtain the weight of the soil alone). Errors in the determined weight of soil are probably small--less than 0.3 g. A range of +/-0.3 g would introduce a range of error in the pore space volume of +/-0.11 cc.

Summation of the above error estimates gives a possible range in error for the calculated volume of pore space of +/-1.43 cc. An increase of 1.43 cc to the mean volume of pore space (2.2 cc) would give a pore space volume of 3.63 cc. Using this value in the equation for calculating the helium in pore space concentration yields a value that differs from the mean concentration of 6241 ppb by -239 ppb. A decrease in the volume of pore space by 1.43 cc would yield a pore space volume of 0.77 cc. Using this volume in equation (93) yields a helium in pore space concentration differing from the from the mean by 1095 ppb. These would seem to represent very large amount of possible errors in the helium in pore space concentrations calculated for the Fiji data especially for a decrease from the mean volume of pore space.

As previously discussed, the non-linear nature of the equation for calculating helium in pore space concentrations precludes using low values for the gaseous pore space volume. Samples containing volumes less than 1.0 cc have been excluded from the Fiji and Long Valley data treatments. If indeed samples contain small amounts of gaseous pore space, a tremendous amount of error can be introduced. A decrease in the volume of pore space by 1.0 cc instead of 1.43 cc, would yield a pore space volume of 1.2 cc. Using this volume in equation (93) yields a helium in pore space concentration of 6739 ppb. This represents an increase from the mean value by 498 ppb. Again, this would represent a very large degree of possible error in the helium in pore space concentrations calculated for the Fiji data. It must be pointed out that in this error analysis, a decrease in the volume of gaseous pore space was not accompanied by a decrease in the volume of soil moisture as might generally occur with the samples.

The above analysis shows an estimated range in error for the mean helium in pore space concentration due to errors in the value used for the volume of pore space of about -239 ppb to +498 ppb. This large amount of error introduced into the data by making assumptions on the volumes of pore space may be real. It is also likely that many of the samples would fall within a smaller range in variation than the above estimate.

Headspace. Error estimates on the amount of headspace in each sample would reflect the assumption made for the Fiji data that the volume of soil collected was 9.0 cc for each sample. This yielded a value for the headspace volume for all the Fiji samples of 3.5 cc. It was discussed above that the amount of error associated with the assumed soil volume may be around +/-1.0 cc. This would also introduce a variation in the headspace volume of +/-1.0 cc. An increase or decrease of 1.0 cc in the volume of headspace would yield helium in pore space concentration that differ from the mean by +/-175 ppb. This is a large amount of error and, as with possible errors in the pore space volumes, creates a large amount of possible variation among the data generated in the Fiji survey, unless most of the samples can be considered to have a smaller variation than +/-1.0 cc in headspace volume.

Laboratory Temperature. A typical room temperature of 22°C was assumed to be the temperature of the Fiji samples at the time of analysis. Actual temperatures of the samples may have varied from this by +/-2.0°C which would give calculated helium in pore space concentrations that differ from the mean by only +/-0.2 ppb. Therefore, even if the temperatures of the samples prior to analysis is different from the approximate value of 22^{o}C, this will not have a significant effect on the calculated helium in pore space concentrations.

Container Pressure. As with the Long Valley samples, the actual pressure existing in the sample container prior to analysis was not directly measured. An approximation of this value was made by calculating what the pressure would have been due to thermodynamic changes within the container. Variations in this calculated pressure would occur if gas production or loss (consumption) occurred in the Vacutainer between the time of collection and analysis. For example, the possibility exists that the samples collected in marine marshes or mangrove swamps may have contained bacteria that produce methane. The degree to which this and similar processes occurs is hard to predict. Again, many of the samples where this may be a problem were not considered in the results due to the lack of sufficient gaseous pore space to allow calculation of helium concentrations by equation (93). A variation of +/-.005 atm from the mean container pressure (.96975 atm) would result in a change from the mean helium in pore space concentration of +/-75 ppb. A smaller variation of +/-.001 atm would result in helium in pore space concentrations that differ from 6241 ppb by +/-15 ppb. A much larger variation of +/-0.01 atm would yield an error estimate of +/-150 ppb. While larger variations would have a more profound effect on the calculated helium in pore space values, gas production or loss may be small except with unusual samples. Since no information on this variation was available, an estimated error range of +/-0.003 atm was used. This would cause a variation in the mean helium in pore space concentration of +/-45 ppb.

Henry's Law Constants. The Henry's law constants that appear in equation (93) are dependent on temperature and the liquid that helium is dissolved in. Henry's Law constants determined for pure water, the average field temperature (30.6^{o}C), and then for the assumed laboratory temperature of 22^{o}C, differ by about 0.015 x 10^{5} mol H_2O/mol He. Varying the Henry's Law constant for either the laboratory or field temperature by 0.015 x 10^{5} yields calculated concentrations of helium in pore space that differ from the mean by about +/-0.7 ppb.

If a sample's soil moisture contains appreciable amounts of dissolved solids, such as in seawater, the Henry's law constant will differ from that determined for helium dissolved in pure water. As salinity is increased, the solubility of helium decreases and temperature has less of an effect on the solubility (Weiss, 1971). Smith and Kennedy (1983) report that the Henry's law constants calculated from low pressure solubility data (25^{o} C) are 1.47 x 10^{-4} atm for helium in pure water and 1.80 x 10^{-4} atm for helium in a 1.003 M NaCl solution. This molarity of sodium chloride is slightly higher than that of sea water. Comparison of these values show a difference in the constants attributable to deviations from fresh, pure water of about $0.3 \cdot 10^5$ mol H_2O/mol He. Varying Henry's Law constant by $0.3 \cdot 10^5$ yield calculated concentrations of helium in pore space that differ from the mean by +/- 14 ppb. The above results gives a value that differs from the mean concentration by +/- 14.7 ppb.

Headspace Concentrations. An idea of the accuracy of the reported helium in headspace concentrations was obtained through comparison of duplicate helium in soil-gas samples sent to Hager Laboratories and the U.S. Geological Survey, Denver. Eleven samples randomly collected during the period of the survey were analyzed. Results are shown in table 9. A regression analysis on the data yielded a correlation coefficient (linear) of 0.831. This suggests that a good degree of accuracy was obtained. A similar comparison could not be done with the soil samples, due to the difficulty in obtaining duplicate samples.

Since a precision of +/-10 ppb was reported for the determined helium in headspace values, this was considered as an estimate of error for these values. Varying the mean helium in headspace concentration (5630 ppb) by +/-10 ppb yields a corresponding variation in the calculated helium in pore space concentration (6241 ppb) of +/-26 ppb. Errors occurring in the measurement of helium in headspace concentrations for Fiji introduce a fair amount of error in the calculated helium in pore space concentrations.

Table 9. Analysis results on duplicate soil-gas samples sent to Hager Laboratories, Denver, and the U.S. Geological Survey, Denver.

U.S.G.S., Denver [He] in ppb	Hager Laboratories, Denver [He] in ppb
637	620
318	390
358	330
358	330
338	330
318	440
379	490
379	330
358	410
557	570

Correlation Coefficient, R = 0.831

<u>Correction of Dilution.</u> Possible errors resulting from the correction for dilution by overpressurizing can also be examined here. As previously examined, the concentration of helium measured in the headspace of a sealed sample must be corrected for the dilution caused by the addition of laboratory air prior to analysis before calculation of helium in pore space concentrations can be done. An accurate concentration of helium in the headspace after dilution is not obtained from the data treatment if equilibration between the gaseous soil pore space of clayey soils and the added air occurs, or if less than 100% equilibration between the gaseous pore space of sandy samples and the added air occurs.

Using the mean values for the Fiji parameters, and a helium in headspace concentration corrected for dilution for a clay soil (0% equilibration), a helium in pore space concentration of 7100 ppb is obtained. Varying the mean volume of gaseous pore space (2.2 cm^3) to reflect what this volume would be if 12.5% (a gain of 0.28 cm^3) of the available pore space did undergo equilibration with the added air and the headspace gas yields a helium in headspace value (5953 ppb) that, when used in the calculation of helium in pore space, yields a decrease of 64 ppb. If 25% of the available gaseous pore space volume undergoes equilibration with the added air a decrease of 116 ppb is obtained. If 50% of the gaseous pore space volume undergoes equilibration, a decrease in the helium in pore space concentration of 206 ppb is obtained. It is probable that if any equilibration of the gaseous pore space of clay samples with the added air does occur it would only be with the very upper amounts of soil. Therefore, an error estimate obtained by using an equilibration percentage of 12.5% instead of 0% equilibration may be reasonable.

Soil samples that are sandy yield a helium in pore space concentration of 6768 ppb when using the mean parameters and a helium in headspace concentrations corrected for dilution by assuming complete equilibration (100%) with the headspace and gaseous pore space volumes. If sandy samples only had 50% (a drop of 1.1 cc) of their gaseous pore space undergo equilibration with the added air (instead of 100% equilibration) a helium in pore space concentration of 6894 ppb is obtained. This represents an increase of +126 ppb. If 75% of the volume of gaseous pore space undergoes equilibration with the added air, the calculated helium in pore space concentration would be 6825 ppb--an increase from the helium in pore space concentration calculated assuming 100% equilibration of 57 ppb. If all but 87.5% of the gaseous pore space volume undergoes equilibration with the added air, a helium in pore space concentraion of 6796 ppb is obtained--an increase of 28 ppb. It may be necessary to conclude that an error estimate on the degree to which the gaseous pore space of the sandy samples collected in Fiji undergo equilibration with the added air is large, since many of the sandy samples that were collected were wet. This would hinder the movement of gases. Additionally, these samples were not agitated on a Vortex stirrer after the addition of the excess air like those collected in Long Valley. Therefore, it may be reasonable to estimate the error associated with dilution by overpressurizing for sandy samples as that arising from the 50% equilibration or +126 ppb.

As previously discussed, the range of time (3 to 8 weeks) between the collection and analysis of the Fiji soil samples appears to fall after significant increases in helium concentrations inside the Vacutainers occurs (due to outgassing of higher helium in the stopper), but before amounts of leakage out of the Vacutainer could have occurred.

Total Error Estimate. Using the larger error estimate for the pore space parameter, the square root of the sum of the squares of the error estimates discussed above would give confidence limits to the mean helium in pore space concentration--6241 ppb at +/-549 ppb. While this indicates that the concentrations of helium in pore space obtained from the raw Fiji data have a high degree of error, it must be noted that the above analysis examines a wide range in variations in the determination of helium concentrations in soil.

DISCUSSION

In the previous section, it was estimated that a typical helium in pore space concentration for the Fiji survey had an associated error of +/-549 ppb. This is a large amount, and arises from the many assumptions that had to be made to allow the calculation of helium in soil pore space values. It is hoped that many of the calculated helium in pore space concentrations would have a much smaller range in error than the above estimate and that the use of the developed equations make the data generated in the Fiji survey more meaningful and useful.

The range in the calculated helium in pore space values is -640 to 4560 ppb. Since the estimated amounts of error are well within this range of values, this suggests that interpretations of helium in pore space results can be made that are significant despite possible inaccuracies, but the high degree of related error suggests using extreme caution in interpreting anomalies in the calculated helium in pore space concentrations. Caution is also indicated in drawing conclusions from the raw data--helium in headspace concentrations because they may not reflect actual helium anomalies, due to many of the factors that have been discussed in this study.

A regression analysis was done to examine possible relations between helium in headspace and calculated helium in pore space concentrations on a point to point basis. The cross plot of helium in headspace versus helium in porespace seemed to indicate a trend towards linearity. The linear regression plot is shown in figure 22. Results of the regression are:

Equation of the line:	$Y = (4.27223)X-17066.6$
Coefficient of determination,	$R^2 = 0.7891$
Coefficient of correlation,	$R = 0.8883$
Standard error of estimate	$= 482.87$

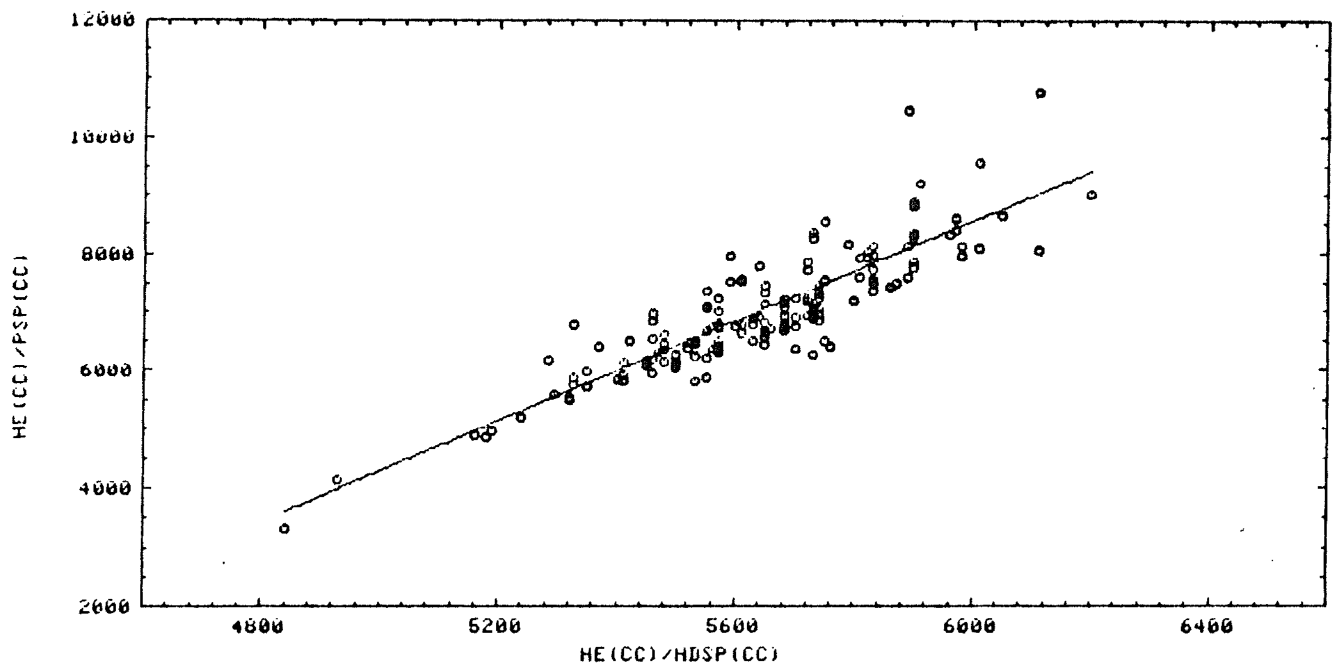

Figure 22. Linear regression analysis of helium in headspace versus helium in gaseous pore space concentrations, Fiji.

Examination of this plot shows that while the correlation coefficient for a linear regression is high between the two (0.888) there does seem to be some scatter in the data about the determined slope. This reflects those samples that are different from the majority, i.e. they contain more water and therefore less porespace. This also suggests that the corrections applied to the raw data through the determination of actual helium concentrations have made a significant difference on a sample-to-sample basis for several of the soils. Helium concentrations for the Fiji survey are higher and show a wider variation than those obtained in Long Valley. This is reflected in the regression plot by less grouping of data around the atmospheric helium concentration of 5240 ppb.

A comparison of the smoothed contour maps for helium in headspace data and helium in pore space data (figures 19 and 21) can be made. It is important to note why smoothed maps were generated instead of using a program that simply contours the available data. A more standard contouring program would tend to create a map with many "bulleyes" of higher and lower areas of helium. This is due to the inherent noise associated with helium concentrations in the natural environment--helium values can vary significantly within a very small area. A contour map of unsmoothed data would look very different from the smoothed plot. Using unsmoothed contouring, the probability of the map of uncorrected helium data having a high degree of similarity to the map of helium in pore space concentrations would be greatly reduced.

This points out the importance of obtaining large numbers of samples from which to base interpretations and an advantage to using smoothed data.

A part of the Fiji survey showing actual locations of samples and corresponding helium in pore space values can serve to show both the effect of smoothing on contour patterns and why it is not wise to overinterpret the results of the contour maps. Figure 23 shows an enlarged section of the overall sampling area--the northwest quadrant. A sample location showing a high helium in pore space value has been singled out for examination. This same location has been identified in the contour map of helium in pore space, figure 21. Examination of the helium values (figure 23) and resultant anomaly patterns in this area (figure 21) shows how a small number of samples can have a large effect on the extent of an anomaly.

The two high values (3036 and 3144) to the southeast of this point are lowered by the nearby lower values (2744 and 1852) so that this whole group falls below the 2960 contour line. As the 2907 ppb sample point is approached, the effect of these low values is diminished and the 2960 contour line is encountered. The two higher values tend to increase the values immediately around the 2907 ppb point causing it to fall inside the 2960 interval. This anomaly extends somewhat to the north from this point as the result of the effect of these higher points, until it drops back down as it approaches the two samples to the north. Thus a fairly large anomaly is controlled by a few distant

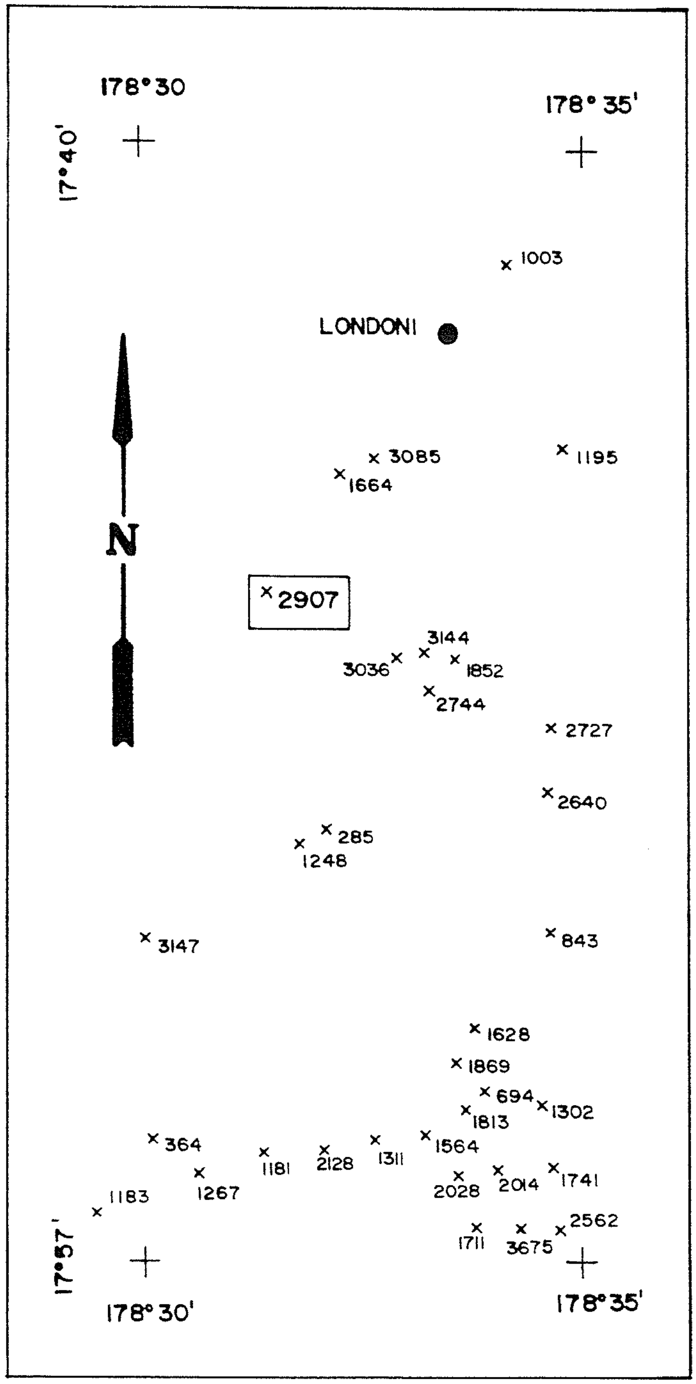

Figure 23. Northwest section of Fiji sampling area, showing sampling locations and helium in pore space concentrations.

points due to the lack of good sample distribution.

A fair degree of similarity in overall patterns of helium concentrations seems to exist between the two contour maps. There are differences in trends, and in some cases, size and degree of anomalies. This could be caused by actual differences that exist between uncorrected and corrected values. As with the regression analysis, this would indicate that the use of the calculations has made a significant difference for at least some of the samples. The wide variation in soil types and moisture contents of the Fiji samples suggest that the calculated concentrations would be important; and that differences between the two sets of results should be observable. Differences that exist between the anomalies patterns from the corrected and uncorrected values also result from the contouring of 16% fewer samples in the helium in pore space map. In this case, sample distribution could account for some of the observable differences in the helium patterns that are discernable between the two.

It has been suggested in the Long Valley Discussion that the magnitude of anomalous values in an area may dictate whether the additional time and expense required to make determinations of actual helium concentrations are needed. In areas of stronger helium emanations, such as Fiji, the anomalous areas may be discernable without doing the corrections. Thus, the high helium concentrations and the similarity that exists between the two anomaly maps of Fiji may suggest that the use of helium in headspace values could be adequate to determine areas of interest (for the period of time over which the survey was carried out).

In summary, the large error associated with calculated helium in pore space concentrations of Fiji suggests caution in their useage but may not negate their utilization. While the higher concentrations of helium generally observed in Fiji indicate that the use of helium in headspace concentrations may be adequate for interpreting the Fiji survey, the corrections do seem to make more than a relative difference in the raw data. These differences may be due to the variation in soil types within the area, and could indicate a necessity for using helium in pore space values, despite the higher observed concentrations of helium.

Implications to Petroleum Occurrences. Despite ambiguities, some inferences can be drawn between the helium survey results and possible petroleum occurrence in eastern Fiji (OEL 7). The observed concentration of helium in the near-surface soils of Fiji depend on the generating source, the modes of transport and degree of retention by transporting and surficial material, and environmental influences.

In temperate climates, meteorological variables such as wind and precipitation events, humidity, air temperature, soil temperature and moisture, barometric pressure and the water table level can have a singificant influence on gas emission from soils. These can vary on a daily or dirurnal basis, or seasonally. Daily and seasonal variations in helium concentrations show a high correlation with variations in soil moisture and soil temperature (Klusman and Jaacks, 1982). With the presence of large amounts of soil moisture or rain, helium in the subsurface, may not readily exchange with the atmosphere, due to a barrier formed by moisture in the overlying soil (a capping effect). Water fills the pore spaces, swells clays and therefore reduces the pathways for helium's exchange with the environment. The result is a build up of helium concentrations in the subsurface.

Since the soils of Fiji in the area of the survey are continually moist, this capping effect may be occurring. Therefore, helium would not undergo significant interaction with the surface environment, and diurnal variations may be minimized.

In the tropical climate of Fiji meteorologic conditions seem to be very constant--temperatures remain relative constant even during rains (table 8), and diurnal variations are minimal (Worthington, 1973). Soil temperatures should be even more constant at the depth of sampling. Therefore, temperature probably does not exert a large diurnal influence on helium concentrations in Fiji. Since meteorologic conditions during the Fiji survey remained fairly constant and soils were generally wet, the assumption was made that diurnal variations were not a major consideration within the survey, and no attempts at corrections for these variations were made.

Examination of the frequency plots (figures 18 and 20) suggest that there are anomalously high samples in both the helium in headspace and helium in pore space data. By visual examination concentrations greater than 800 or possibly 700 ppb (above helium in air) may be anomalously high for the helium in headspace concentrations. This would represent 7 and 15 samples respectively. Visual examination of the helium in pore space concentrations suggests that values greater than 3360 ppb or possibly 2960 ppb may be anomalous. This would represent 10 and 19 samples respectively. Using the mean plus two standard deviations (2.5% of values) to identify anomalous concentrations yields concentrations greater than 848 ppb for helium in headspace (15 samples) and greater than 3823 ppb for helium in pore space (5 samples).

Examination of the contour maps show where these areas of higher concentrations occur. Helium in headspace concentrations exhibit higher values in the Kamba Point region, at a small area approximately 17 km north of Suva, and at a larger area 7 to 10 km south of Londoni. Note that with the possible exception of the northern most area these anomalies are generated by the presence of only a few samples of higher helium concentrations. The helium in pore space map also shows the occurrence of higher concentrations south of Londoni, and in the Kamba Point region. The area of higher helium concentrations north of Suva appears to be more extensive on this map than the former, and a small area approximately 5 km south of Kumi seems to show more emphasis than on the helium in headspace map. The Kamba Point area has reported the existence in former years of "kerogen" leaks, which may represent the leakage of higher distillate hydrocarbons. This suggests a possible positive correlation between helium values in survey and petroleum occurrences.

The geology of the area of OEL 7 can be examined for possible correlations with the observed helium concentrations. From Suva northward past Nausori sediments and rocks are generally composed of recent unconsolidated silt, clay, sand, and gravel, with some Miocene sandstone and marls. North of Nausori and Kamba Point rocks are mostly Plio-Pleistocene basalt flows and volcaniclastics (Phillips, 1965). Faults (and geothermal features) are not common over the area of the survey and should not complicate interpretation of the helium results. The anomaly patterns observed on both maps do not seem to show any obvious correlation to the geology of the area, with the possible exception of the northern most area of higher helium concentrations. Igneous basalts underlying this area may contain higher amounts of radioactive minerals than units to the south. If this is the case, they could generate larger amounts of helium that, when detected at the surface, may not be indicative of petroleum occurrences, but would be a regional pattern.

It has been mentioned that the offset of helium anomalies by ground water flow has been observed in other surveys. If this phenomenon occurred in Fiji, anomalies should be offset to the east--towards the ocean. The degree to which such offset occurs is small--often less than 0.5 km. At the scale of the Fiji contour maps displacement of anomalies by ground water flow showed not be significant.

The contour maps of figures 19 and 21 also show the approximate locations of drilling sites. The onshore geology in this area indicates the presence of sandstone and marl units. While other forms of geologic and geophysical data must also be used for the correct interpretation of the potential of this area, some tentative conclusions can be drawn from the helium results. This area represents a region of lower values on the helium in headspace map. The helium in pore space map shows some higher values in this area and may be an example of an area where the corrections introduced in this study have made a difference in observed anomalies.

A contour interval of 800 ppb was used on the helium in pore space map. Even with the large degree of error estimated for these results, helium values in the drilling locations area while not highly anomalous, may be somewhat higher than average. But caution must be used here in the interpretation due to the small number of samples that are determining anomaly patterns in the area. Other areas that show larger helium anomalies for both helium in headspace and helium in pore space may be more favorable for drilling consideration. It would be of interest and utility to go back into this area and do a much more detailed helium survey, using a closer sampling grid, and measuring necessary parameters to allow the accurate calculation of helium in pore space concentrataions. This would give a much more definitive idea of the helium emission in this area. The test of the helium survey would then be the drilling projects. Again, the helium survey must be used in conjunction with other information for a correct interpretation of the source of an anomaly.

RECOMMENDATIONS

The results from the Long Valley and Fiji surveys indicate a need for more studies on the use of soil (and water) samples. For exploration considerations, further studies would help determine whether the gain in confidence in the data generated from the use of these corrections offsets the cost.

Some recommendations can be made as to how to improve the techniques that were used in both Long Valley and Fiji to allow determinations of actual concentrations. Future surveys should thoroughly examine the methods proposed for collection and analysis prior to conducting sampling.

The need arises for the collection of larger amounts of sample. This would avoid the problem of having such small pore space volumes that samples must be removed from consideration. Additionally, the collection of larger amounts of samples would lessen errors associated with the calculated concentrations since errors in the measurement of pore space and headspace would have less of an effect. This suggests finding alternatives to using Vacutainers for sample collection. Containers chosen for usage should be impervious to gas leakage.

Allowing a constant amount of time to elapse between the collection and analysis of samples would yield greater confidence in reported helium in headspace concentrations with a chosen container.

The depth that samples are collected from is an important consideration. Samples should be collected deep enough to avoid surficial environmental influences. The Fiji and Long Valley soil samples were collected 12-45 cm from the surface. While this sampling depth probably did not introduce errors into these surveys, a deeper depth of sample collection would be recommended.

Further studies are needed to determine appropriate amounts of time that soil samples should be allowed to equilibrate between collection and analysis. Samples should be analyzed after a maximal concentration of helium appears in the headspace gas. This equilibration period would vary with soil type--clayey samples needing a longer period than sandy samples. Placement of samples in mixing devices, such as ultransonic cleaning baths, should hasten equilibration, allowing analysis to be performed sooner after collection.

Since equilibration between helium in the soil moisture, gaseous pore space and gaseous headspace is temperature dependent, it should be allowed to occur at a constant and known temperature for the determined period of time.

The addition of excess air to samples prior to analysis (to overpressurize them) should be avoided. Thus, approximations to correct for the dilution this causes need not be made. This could be circumvented by fitting a 3-way value onto the syringe used for extracting headspace gas prior to instrument analysis. The needle is inserted through the sample septum or rubber stopper, and an appropriate amount of headspace gas is drawn into the syringe. Closing of the valve traps the gas sample within the syringe; the needle can then be withdrawn from the sample without additional air being drawn into the syringe containing the underpressured sample. The needle is then inserted through the septum on the mass spectrometer, and the valve is opened to release the gas into the instrument.

The pressure inside a contained sample prior to sample analysis should be measured, rather than calculating what it would be based on thermodynamic considerations (as in Fiji and Long Valley). This could be done by inserting a needle through the sample stopper or septum which is hooked to a low-volume pressure gauge. Analysis of headspace gas would be done immediately afterwards.

A better method of determining soil pore space than the vacuum system used for the Long Valley samples should be employed. There are obvious errors in this method, especially since the pore space being measured is not that of the original soil, but of a disturbed sample. Additionally, this technique is only amenable to some soil types. Several methods are discussed in soil science literature as to the measurement of soil porosity or air filled porespace. A method more applicable to soil helium surveys involves the determination of the volume weight of a soil sample, from which the total percentage pore space present in a soil is calculated. The volume weight of a soil expresses the actual weight of dry soil in any given volume, and indicates the number of times heavier the dry soil is than water occupying the same total volume. This differs from specific gravity of a soil which compares the weight of the dry soil to that of water that will only occupy the same volume as the particles alone.

A volume weight of a soil can be obtained by driving a cylinder of known volume into the ground and obtaining a core of natural soil. By weighing the soil and determining the amount of water that it contains (drying in a 100°C oven), the amount of absolutely dry soil may be determined. Dividing this by the weight of an equal volume of water gives the figure for the volume weight. (Frosterus and Frauenfelder, 1926). A rubber-tube method has also proved convenient for the field determination of volume weight, whereby a hole is bored in the soil to the required depth by a specially constructed auger, the soil then being carefully removed and later oven-dried. A tubular rubber bag of the size of the auger hole is carefully inserted into the bored hole. The bag is then filled with water to the level of the soil surface. The volume of water is measured and therefore the volume of the soil removed is determined. Knowing the weight of the dry soil and its original volume, the volume weight may be calculated. The experimental error is reported to be low (Israelson, 1918). Clay, clay loam, and silt loam surface soils may range from 1.00 to as high as 1.60 in volume weight, while a variation from 1.2 to 1.8 can be found in sands and sandy loams (Harland, and Smith, 1928).

After measurement of the volume weight of soil, the volume of water, and the volume of the soil particles is determined. The volume of the soil particles is measured by taking the weight of the dry sample and dividing by the specific gravity of the soil, which can be experimentally determined (for example using a picnometer) or by considering an average arable surface soil as having a specific gravity of 2.65. The percentage of porespace in a soil can then be found by:

$$\% \text{ porespace} = 100 - \left(\frac{\text{vol. wt}}{\text{sp.gr.}} \times \frac{100}{1}\right) \qquad (110)$$

As discussed in the Evaluation of Errors, Fiji section, sandy surface soils generally show a porosity range of from 35 to 50 percent while heavy soils vary from 40 to 60 percent or perhaps even more in cases of high organic matter (Lyon and Buckman, 1943). Pore space also decreases with depth. Once the percentage of total pore space is obtained, subtraction of the percentage of pore space occupied by the volume of water yields the volume of gaseous porespace.

While the explorationist may hesitate to measure the additional parameters necessary to allow determinations of helium concentrations, the following should be noted.

1. As was discussed in interpretation of the Long Valley results, if an area contains varying types of soil, and varying amounts of water, it is possible that helium in headspace concentrations may

be inadequate for making interpretations, since the raw data may reflect sample variations instead of geologic features. This would suggest useing corrected helium concentrations. If samples show a high degree of uniformity, such as the dry soils of Long Valley, the use of helium in headspace data may be sufficient.

2. Again, the use and importance of the corrections may depend on the size of an area under consideration. For example, either of the contour maps generated in the Fiji survey might be of use in distinguishing between areas of helium highs and lows within a 20 km radius. If it is desired to use helium to help identify anomalous areas on a smaller scale, use of the corrections may become very important, since the calculation of helium in porespace could make significant differences on singular samples.

3. The magnitude helium emanations in an area can help determine the need for determining actual helium concenetrations. In an area where emanations are large, such as in Fiji, corrections may be of less importance. In surveys where the more common case of weaker, more subtle anomalies are observed as in Long Valley, differences created by the use of calculated concentrations, may become very important in the establishment of anomalous values.

4. If it is desired to later repeat a survey in an area, the use of calculated helium concentrations would be important, since environmental variables such as soil moisture can change between surveys.

5. The calculation of helium in pore space concentration would be very important if a comparison and correlation between two different areas is desired.

In any helium survey, whether raw data or corrected is used, the following considerations should be made:

1. The possibility of false anomalies due to atmospheric variations must be guarded against.
2. It is a good practice even when the determining helium in soil concentrations to collect similar sample types to avoid introduction of extraneous errors.
3. In some areas, it may be important to establish the background helium concentrations, instead of assuming a constant background of atmospheric helium. Statistics can be used to separate background from anomalous populations. The collection of similar sample types (similar soils) can help avoid differing background concentrations.
4. As frequently stated, it is important that interpretation of helium surveys be coupled with geophysical and geological investigations to help determine the source of anomalously high helium concentrations. In turn, helium surveys can help in the determination of whether geophysically and geologically determined structures may contain oil and gas deposits.

The calculation and corrections presented in this study to allow the determination of helium concentrations in soils and water allow a more accurate representation of data to be obtained, instead of only relative measurements. While these corrections are possibly of lesser importance in the exploration of some areas, they are probably very significant in others and allow comparisons to be made between different surveys and different areas.

It should be noted that soil-gas concentrations obtained by direct probe measurements are not exactly equivalent to soil-gas concentrations calculated from soil sample analyses. The calculated concentrations would be higher. The reason for this is unknown but does not reflect an error in the equations, since actual amounts of helium in container headspace are higher than soil-gas measurements. This may arise from some mechanism causing the release of additional helium in soils that is not picked up by the use of probes, or probe collection may cause a dilution of the helium.

Previous studies have indicated that helium can be a valuable tool in exploration. Like any new method, the technique needs development to be properly used and understood. It is likely that even further improvements can be added to the material presented here, and that secondary corrections of lesser magnitude may be added to the determination of helium concentrations. These would depend on time and equipment needed for the measurement of such.

SUMMARY AND CONCLUSIONS

High concentrations of helium in the near surface environment have been found to be associated with petroleum occurrences, uranium deposits, and geothermal areas. This has prompted its use as an exploration tool.

The Fiji islands may contain oil and gas deposits. As part of an exploration program in this area, a helium survey was conducted. The wet, clayey soil conditions in Fiji did not allow the collection of soil-gas samples--a direct method of measuring subsurface helium concentrations. Therefore, soil samples were collected. Helium in gaseous headspace analyses were performed on these samples. This is only a relative measurement of the helium concentration. Since the utility of helium surveys could be increased by the collection and use of soil samples, a study of whether these values mirror actual helium in soil concentrations was undertaken.

Equations are presented in this study that allow the calculation of actual concentrations (in soils and waters) using measured concentrations of helium in headspace. These calculations allow more accurate determinations of helium to be made, but require the measurement of additional parameters. This results in added time and cost in a survey.

These calculations, or corrections, were used on a helium in soils survey conducted in the Long Valley geothermal area. Significant variations between anomaly patterns for the uncorrected data (helium in headspace) and the corrected data (helium in pore space) were not observed. The similarity exhibited may be due to the soil and climatic conditions in this area.

A smoothing of contour lines on the corrected helium data was observed. This is proposed to be due to a reduction in noise inherent in uncorrected helium in headspace data. An error analysis was then conducted on the helium in pore space data, indicating a high confidence level for the data.

Parameters that occur in the equation for calculating helium concentrations in soils were examined to identify those which have the greatest effect on concentrations. It was determined that gaseous pore space volumes, headspace volumes and helium in headspace concentrations must be accurately measured to ensure accuracy in determinations. Other parameters such as soil moisture, and soil temperature have lesser effects.

Using approximations on parameters not measured, an evaluation of the Fiji data was done by calculating helium-in-soil-pore-space concentrations. A large amount of error was found to be associated with the calculated concentrations, but some conclusions were drawn as to the utility of these corrections in Fiji. The anomaly patterns between the uncorrected and corrected data do exhibit differences. This difference may be the result of variations in sample distribution, but probably also reflects changes incurred by the use of the calculated values.

The conditions of a survey may dictate when the corrections presented here are necessary for accurate interpretations to be made. If soil types (hence porosity) and moisture contents vary in an area, the use of the equations can become very important. If helium in headspace values are to be used, the same amount of soil must be collected with each sample. This can be difficult to accomplish with soils such as clays, and can indicate a need for the use of corrected concentration. The helium emanations in an area could dictate whether calculated concentrations should be used. Corrected values may be of less importance in areas of strong emanations. The overall importance of doing these corrections could depend on the size of an area under prospecting considerations. If the survey is being used to distinguish areas of high and low concentrations over a large area, the corrections may be of lesser importance. If distinctions are to be made on a small area, differences caused by the corrections on a point to point can become much more significant. While the collection of a large number of samples is desirable for any helium survey, the corrections can become very important when fewer samples are collected. In these cases, the calculated values should lend a higher confidence level to results.

Some suggestions for improvements to techniques for determining actual helium in soil concentrations are given. These include the selection of appropriate containers, the collection of large number of samples, deeper soil sample collection, consideration of equilibration times, the measurement of container pressures, avoidance of sample dilution, and the accurate measurement of pore space and headspace volumes, and helium in headspace gas concentrations.

While more studies are needed, the use of these equations for calculating helium concentrations may be a preferred method of conducting helium surveys, yielding greater confidence in results and interpretations. As exploration targets become harder to find, techniques such as helium surveys increase in importance and use. Used in conjunction with other available data, such surveys can be powerful exploration tools.

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Appendix A

Experimentally determined Henry's constants for helium, a graph of these constants vs. temperature, fitted with a 4° polynomial regression, and the equation for this curve.

Table A-2. Experimentally Determined Henry's Law Constants for Helium (CRC Handbook, 1951-52)

$K = P/X$
P = partial pressure mm of Hg
X = mole fraction

T(°C)	T°(K)	K x 10^{-7}
0	237.16	10.0
10°	283.16	10.5
20	293.16	10.9
30	303.16	11.1
38	311.16	11.0
40	313.16	10.9
50	323.16	10.5
60	333.16	10.3
70	334.16	9.88

A fourth order polynomial equation was fit to the experimental K_{He}'s in Table A-2 to facilitate determination of K_{He} for a given temperature, T (^{o}C). A graph of this equation appears on A-4. This equation is used solely as an aid to extrapolation between known data values and does not imply adherance to a physical model.

$$K_{He} = 10.002 + 4.1939.10^{-2}T + 1.297 .10^{-3}T^{2} - 6.6098 . 10^{-5}T^{3} + 5.4693.10^{-7}T^{4}$$

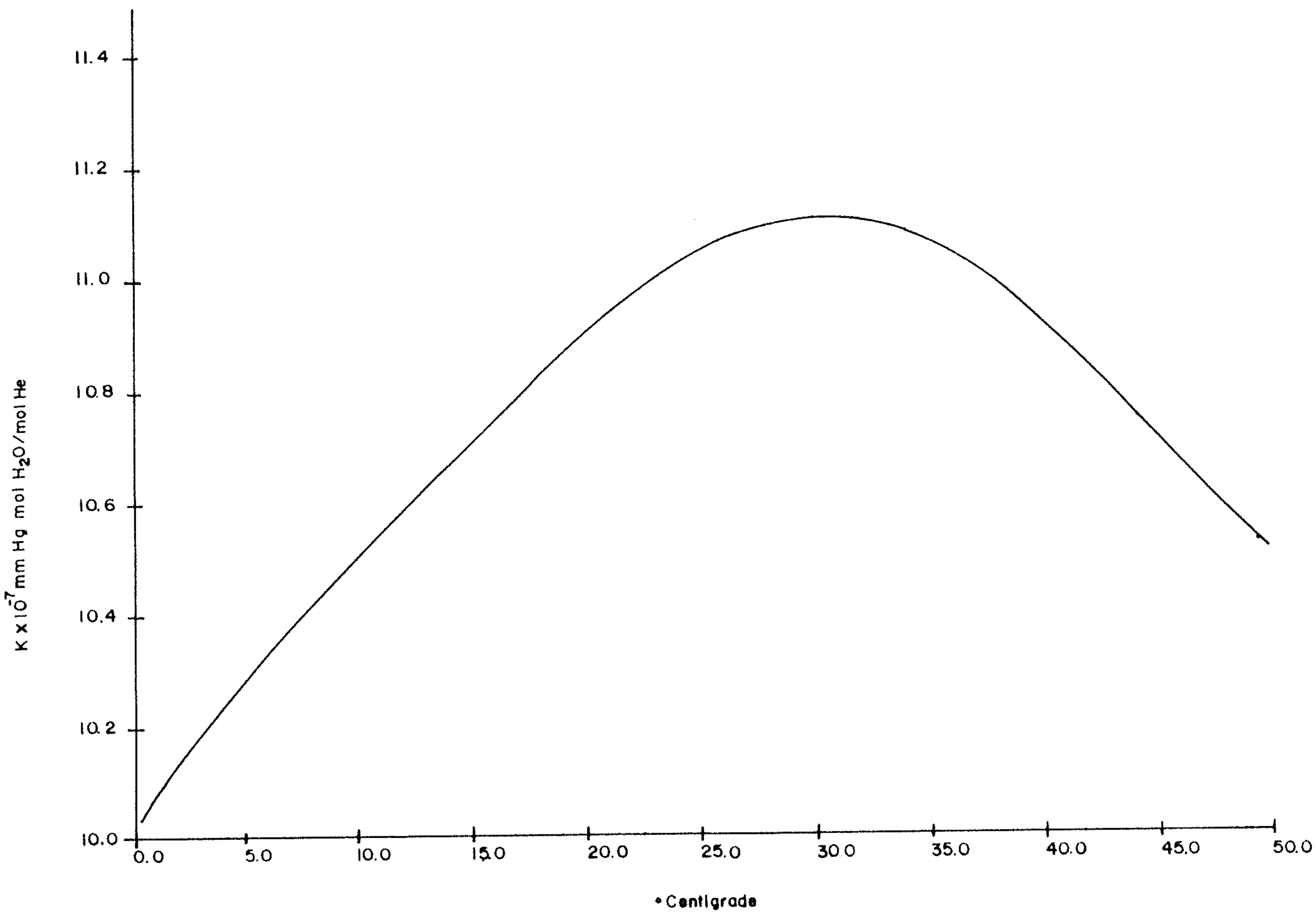

Figure A-4. Graph of Henry's Law constants versus temperature, curve fitted by a order degree polynomial equation.

APPENDIX B

Data from the Long Valley helium survey.

Pages B-3 through B-7 contain tables of sample numbers and latitude and longitude (in degrees) of sampling sites.

SAMPLE	LATITUDE	LONGITUDE
221	37.6869	118.7947
163	37.5894	118.8522
193	37.6292	118.9581
192	37.6350	118.9667
231	37.6922	118.8836
242	37.6981	118.9361
238	37.6975	118.9256
189	37.6275	118.9953
225	37.6994	118.8339
240	37.7172	118.9256
239A	37.7056	118.9089
241	37.7225	118.9061
224	37.6917	118.8378
227	37.6800	118.8258
2.06	37.6292	118.7711
260	37.6500	118.9000
191	37.6306	118.9736
285	37.6603	118.8283
230	37.6744	118.8919
223	37.6914	118.8236
202B	37.6350	118.7444
194	37.6275	118.9456
235	37.6769	118.9017
229	37.6756	118.8500
201	37.6336	118.7967
232	37.7028	118.8964
197	37.6222	118.9167
233	37.6569	118.9117
200	37.6419	118.9031
199	37.6167	118.9073
195	37.6283	118.9356
254	37.7122	118.9033
251	37.7242	118.8317
196	37.6281	118.9272
253	37.6914	118.8961
198	37.6228	118.9078
252B	37.7083	118.8200
250	37.7144	118.8422
245	37.7264	118.8747
278	37.6589	118.9369
226	37.6875	118.8478
255B	37.7111	118.8914
247	37.7081	118.8631

SAMPLE	LATITUDE	LONGITUDE
247	37.7081	118.8631
239B	37.7056	118.9089
286	37.6528	118.8350
205	37.6317	118.7883
258	37.6753	118.8583
252A	37.7083	118.8200
259	37.6625	118.8794
290	37.6586	118.7525
249	37.6958	118.8556
255A	37.7111	118.8914
274	37.6733	118.9911
256	37.7083	118.8794
203	37.6378	118.7583
267	37.6933	119.0256
190A	37.6283	118.9794
276	37.6528	118.9433
277	37.6458	118.9294
257	37.6883	118.8603
270	37.6731	119.0064
272	37.6917	119.0003
275A	37.6619	118.9867
275B	37.6619	118.9867
269A	37.6825	119.0033
204	37.6219	118.7561
288	37.6475	118.7308
246	37.7194	118.8608
287B	37.6439	118.8494
279	37.6647	118.9500
271	37.7000	118.9953
280	37.6758	118.9675
287A	37.6439	118.8494
282	37.6864	118.9881
190B	37.6283	118.9794
281	37.6722	118.9747
268	37.6822	119.0183
273	37.6811	118.9939
265B	37.7119	119.0375
283	37.7383	118.8433
248	37.6975	118.8647
289	37.6536	118.7625
261	37.6522	118.8947
262	37.6764	118.9189
265A	37.7119	119.0375
264	37.7164	118.9889

SAMPLE	LATITUDE	LONGITUDE
266	37.7044	119.0275
284	37.6636	118.8192
263	37.7361	118.9222
269B	37.6825	119.0033
164	37.6228	118.8625
182	37.7247	118.8128
168	37.7486	118.9217
177	37.7331	118.9044
184	37.7139	118.8164
176	37.7464	118.9028
181	37.7369	118.8211
175	37.7222	118.9522
173	37.7294	118.9461
174	37.7211	118.9389
180	37.7383	118.8417
172	37.7261	118.9558
170	37.7664	118.9442
186	37.6614	118.8092
185	37.6833	118.8117
179	37.7431	118.8636
167	37.7653	118.9667
153	37.5575	118.7169
157B	37.5669	118.6942
156	37.5608	118.6633
149	37.5597	118.7394
151	37.5767	118.7667
147B	37.5714	118.7850
145	37.5989	118.8000
146	37.5864	118.7844
171	37.7419	118.9525
135	37.7000	118.9528
143	37.6222	118.8375
148	37.5797	118.7619
144	37.6175	118.8214
142	37.6339	118.8747
147A	37.5714	118.7850
150	37.5706	118.7533
141	37.6378	118.8861
138	37.6581	118.9533
139	37.6456	118.9533
152	37.5633	118.7742
183A	37.7089	118.8083
183B	37.7089	118.8083
178	37.7431	118.8814

SAMPLE	LATITUDE	LONGITUDE
116	37.6494	119.0161
133	37.7142	118.9972
132	37.7369	119.0267
130	37.7297	118.9942
129	37.7633	118.9944
126	37.7319	118.9653
127	37.7472	118.9797
124B	37.7083	118.9500
124A	37.7083	118.9500
123	37.6989	118.9475
122	37.6897	118.9417
121	37.6806	118.9319
120	37.6661	118.9247
117	37.6506	119.0247
118	37.6508	119.0364
137	37.6806	118.9508
119	37.6467	118.9167
136B	37.6906	118.9553
131	37.7400	119.0119
140	37.6411	118.9375
114B	37.6528	119.0000
112	37.6122	119.0086
113	37.6542	118.9883
108B	37.6247	119.0056
110	37.6108	119.0003
111	37.6056	119.0006
109	37.6167	119.0006
105	37.6444	118.9914
106	37.6389	118.9953
107	37.6308	119.0000
108A	37.6247	119.0056
103	37.6492	118.9828
102	37.6486	118.9750
104	37.6447	118.9833
100A	37.6461	118.9644
100B	37.6461	118.9644
101	37.6472	118.9697
115	37.6500	119.0083
134	37.7033	118.9689
114A	37.6528	119.0000
214	37.7089	118.7700
213	37.6989	118.7625
211	37.6692	118.7811
215A	37.7269	118.7833

SAMPLE	LATITUDE	LONGITUDE
209	37.6447	118.8000
136A	37.6906	118.9553
157A	37.5669	118.6942
165A	37.6236	118.8853
207	37.6442	118.8417
217	37.7489	118.7314
218	37.7333	118.7486
216	37.7414	118.7636
208B	37.6378	118.8583
208A	37.6378	118.8583
210	37.6544	118.7917
215B	37.7269	118.7833
237	37.6914	118.9158
220	37.6967	118.7828
243	37.7206	118.9047
236	37.6833	118.9131
161	37.5822	118.7325
158	37.5669	118.6942
169B	37.7472	118.9394
165B	37.6236	118.8853
160	37.5722	118.7250
159	37.5717	118.7050
162	37.6083	118.8494
188	37.6333	118.8108
163	37.5894	118.8522
166	37.6256	118.8981
187	37.6497	118.8092
125	37.7192	118.9558
128	37.7544	118.9850
169A	37.7472	118.9394
154	37.5594	118.6981
155	37.5617	118.6828
219	37.7350	118.7622
221	37.6869	118.7947
234	37.6678	118.9047
222B	37.6775	118.8000
228	37.6847	118.8622
222A	37.6775	118.8000

The following table presents the measured volumes of pore space and headspace for each sample, the amount of air added prior to analysis, the measured concentration of helium in the headspace, the concentration of helium in headspace corrected for dilution and the difference (in ppb) between the two concentrations.

Sample No.	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air (cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
221	5.0	-0.03	5	5358	5476	118
163	7.8	5.71	5	5032	4955	-77
193	5.8	5.53	5	5258	5266	8
192	12.7	-0.38	5	4945	4825	-120
231	7.1	5.18	5	5343	5385	42
242	8.4	4.70	5	5281	5297	16
238	6.9	6.22	5	5255	5260	6
189	9.4	5.59	5	5252	5256	4
225	6.7	4.99	5	5261	5270	9
240	6.9	5.12	5	5412	5484	72
239A	4.8	7.14	5	5272	5285	13
241	5.8	7.23	5	5326	5359	33
224	7.8	5.01	10	5623	5922	299
227	5.5	7.47	5	5240	5240	0
2.06	5.6	6.60	5	5246	5249	3
260	6.4	6.72	5	5272	5284	12
191	8.7	7.56	5	5297	5315	18
285	5.9	6.63	5	5240	5240	0
230	6.5	7.76	10	5368	5457	89
223	4.2	9.02	5	5317	5346	29
202B	4.7	6.71	5	5272	5286	14
194	7.0	5.35	5	5272	5285	13
235	7.9	5.31	5	5447	5526	79
229	9.5	4.52	5	5336	5370	34
201	6.9	6.15	5	5240	5240	0
232	6.4	6.76	5	5368	5416	48
197	5.7	7.80	5	5240	5240	0
233	7.3	6.61	5	5240	5240	0
200	6.7	4.29	5	5240	5240	0
199	5.8	7.13	5	5254	5259	5
195	5.8	8.53	5	5240	5240	0
254	7.8	5.41	5	5390	5447	57
251	5.2	6.60	5	5254	5260	6
196	6.3	6.73	5	5223	5216	-7
253	6.9	5.92	5	5377	5430	53
198	5.9	6.16	5	5261	5269	8
252B	6.4	6.76	5	5103	5052	-52
250	4.3	8.05	5	5213	5202	-11
245	5.5	6.27	5	5257	5264	7
278	4.6	7.71	5	5216	5206	-10
255B	6.1	5.89	10	5377	5490	114
247	5.3	7.94	5	5377	5428	52
239B	4.8	7.54	5	5240	5240	0
286	4.0	5.98	5	5274	5291	17

Sample No.	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air (cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
205	6.1	7.59	5	5223	5217	-6
258	5.9	6.13	5	5461	5553	92
252A	8.2	5.27	5	5103	5053	-51
259	4.9	5.44	5	5479	5595	116
290	4.5	7.18	5	5258	5266	8
249	6.4	6.82	5	5422	5490	69
255A	7.6	4.74	5	5530	5648	118
274	6.0	6.16	5	5167	5138	-30
256	6.3	5.93	5	5472	5568	95
203	5.9	6.13	5	5276	5291	15
267	7.5	3.65	5	5385	5451	65
190A	6.9	5.85	5	5327	5361	34
276	7.2	5.78	5	5385	5441	56
277	5.4	6.34	5	5422	5499	73
257	5.4	5.84	5	5294	5319	24
270	9.5	4.02	5	5113	5066	-47
272	8.7	4.26	10	5349	5433	84
275A	6.8	6.02	5	5367	5417	50
275B	6.2	5.79	5	5331	5368	38
269A	10.7	3.14	10	5284	5315	32
204	5.4	5.57	5	5226	5219	-7
288	4.7	6.51	5	5247	5251	3
246	5.7	6.70	5	5305	5332	26
287B	10.2	-0.65	5	5186	5157	-29
279	6.1	5.29	5	5385	5449	64
271	9.3	4.29	5	5167	5141	-27
280	7.2	4.78	5	5400	5466	67
287A	10.2	-0.15	5	5240	5240	0
282	8.6	4.37	10	5385	5497	112
190B	6.3	4.23	5	5294	5320	26
281	7.9	5.11	5	5367	5416	49
268	5.8	5.23	5	5313	5346	33
273	6.8	6.52	5	5414	5480	65
265B	7.1	6.28	5	5385	5439	54
283	5.7	7.30	5	5240	5240	0
248	5.3	8.74	5	5429	5496	67
289	5.5	5.27	5	5240	5240	0
261	8.9	5.10	10	5400	5514	114
262	6.3	7.73	5	5240	5240	0
265A	6.9	7.02	5	5294	5314	20
264	9.5	6.32	5	5291	5307	16
266	8.6	6.57	5	5385	5433	48
284	3.3	6.66	5	5240	5240	0
263	9.1	5.43	5	5400	5455	55

Sample No.	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air (cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
164	2.7	10.33	5	5254	5259	5
182	3.5	8.69	5	5281	5298	17
168	5.2	8.60	5	5226	5221	-5
177	7.2	7.48	5	5418	5479	61
184	5.9	9.96	10	5377	5463	86
176	5.9	6.63	5	5295	5317	22
181	3.4	8.09	5	5284	5303	19
175	7.0	8.25	5	5322	5349	27
173	5.8	8.73	5	5254	5258	5
174	6.9	7.82	5	5487	5570	84
180	5.4	9.07	5	5267	5277	9
172	8.7	7.26	5	5432	5492	60
170	6.3	7.43	5	5377	5427	50
186	4.6	7.81	5	5295	5317	22
185	5.4	7.84	5	5240	5240	0
179	5.6	5.90	5	5594	5748	154
167	3.1	5.83	5	5226	5219	-8
153	4.0	7.78	5	5281	5299	17
157B	3.7	0.25	5	5569	5980	411
156	4.9	8.14	5	5309	5335	26
149	2.2	9.84	5	5271	5284	13
151	4.7	5.61	5	5271	5286	15
147B	3.7	8.12	5	5286	5306	20
145	4.5	5.98	5	5609	5785	176
146	3.5	6.29	5	5271	5287	16
171	5.6	9.40	5	5240	5240	0
135	7.1	6.28	5	5455	5536	80
143	4.4	6.78	5	5240	5240	0
148	3.1	9.33	5	5289	5309	20
144	3.5	-0.51	5	4932	4419	-513
142	2.6	9.03	5	5332	5372	40
147A	3.2	7.33	5	5286	5308	22
150	7.6	8.58	5	5271	5280	10
141	2.7	7.27	5	5288	5312	24
138	5.8	8.23	5	5369	5414	46
139	2.8	9.16	5	5291	5313	21
152	2.3	9.67	5	5286	5305	19
183A	3.8	6.65	5	5271	5285	15
183B	3.1	8.43	5	5302	5328	27
178	3.5	6.49	5	5302	5332	31
116	8.1	7.07	10	5392	5493	100
133	6.5	9.76	5	5288	5303	15
132	4.7	7.11	5	5336	5377	41
130	7.5	7.48	5	5417	5475	59
129	3.5	9.99	5	5401	5460	60

Sample No.	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air (cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
126	8.3	8.50	5	5304	5323	19
127	4.5	7.98	5	5449	5532	84
124B	6.4	6.62	10	5481	5666	185
124A	6.0	7.16	5	5342	5380	38
123	3.8	8.15	5	5464	5557	93
122	3.7	8.42	5	5359	5408	49
121	5.2	6.80	5	5274	5288	14
120	4.9	9.64	5	5396	5450	54
117	5.4	9.64	10	5376	5466	90
118	7.3	8.51	5	5308	5329	21
137	6.3	6.93	5	5240	5240	0
119	3.7	8.05	5	5206	5192	-14
136B	6.3	8.53	5	5401	5455	54
131	7.4	7.51	5	5208	5197	-11
140	3.8	10.15	5	5256	5262	6
114B	7.6	3.38	10	5477	5693	216
112	7.9	7.81	5	5376	5419	43
113	5.6	10.10	5	5189	5173	-16
108B	6.9	8.25	5	5382	5429	47
110	6.9	11.12	5	5172	5153	-19
111	6.4	7.56	5	5206	5194	-12
109	9.2	6.96	10	5409	5514	105
105	8.7	6.26	5	5240	5240	0
106	6.6	7.59	5	5511	5606	95
107	8.3	7.50	5	5359	5396	38
108A	7.9	7.41	10	5409	5520	111
103	7.3	8.01	5	5359	5397	39
102	8.8	4.30	5	5613	5755	142
104	5.8	7.13	5	5409	5475	66
100A	7.4	6.91	10	5802	6196	393
100B	6.6	7.59	10	5525	5725	200
101	7.2	5.78	5	5332	5367	35
115	7.5	7.25	5	5257	5263	6
134	6.9	6.85	5	5443	5517	74
114A	6.4	7.06	5	5579	5704	125
214	4.3	4.95	5	5643	5862	219
213	4.7	5.31	5	5240	5240	0
211	7.8	4.51	10	5760	6183	423
215A	3.7	7.35	5	5250	5255	5
209	4.9	5.37	5	5310	5344	34
136A	7.5	7.05	5	5313	5338	25
157A	5.4	0.07	5	5344	5439	95
165A	5.4	6.74	5	5214	5203	-11
207	3.7	7.35	5	5240	5240	0
217	3.5	7.49	5	5234	5231	-3

Sample No.	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air (cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
218	5.8	6.53	5	5270	5282	12
216	2.2	7.77	5	5240	5240	0
208B	4.8	8.24	5	5228	5224	-5
206A	5.9	6.86	5	5210	5199	-12
210	2.3	8.97	5	5219	5210	-9
215B	4.6	7.21	5	5169	5139	-30
237	4.3	7.95	5	5228	5223	-5
220	5.3	6.94	5	5210	5198	-12
243	6.4	6.46	5	5373	5424	52
236	4.3	7.45	10	5329	5404	76
161	5.1	6.67	5	5084	5018	-66
158	7.5	5.98	5	5651	5803	152
169B	7.0	6.38	5	5344	5383	39
165B	5.3	7.94	5	5240	5240	0
160	3.4	9.39	5	5292	5312	20
159	4.4	9.38	5	5266	5275	9
162	3.9	7.22	5	5292	5315	23
188	3.5	8.22	5	5396	5463	67
163	6.1	7.43	5	5032	4955	-77
166	5.4	7.70	5	5266	5276	10
187	4.9	7.51	5	5448	5532	84
125	6.4	8.06	5	5253	5258	4
128	4.0	8.28	5	5500	5606	106
169A	4.9	7.41	5	5370	5423	53
154	2.9	8.63	5	5279	5296	17
155	4.4	7.08	10	5240	5240	0
219	3.6	8.06	5	5370	5425	56
221	5.0	-0.03	5	5358	5476	118
234	5.4	6.14	5	5402	5473	71
222B	5.4	5.77	5	5270	5283	13
228	6.7	6.59	5	5329	5362	33
222A	6.9	5.52	5	5228	5223	-5

The following table contains data on the measured parameters for the Long Valley survey and report the calculated helium in pore space concentration for each sample.

SAMPLE NO.	SOIL TEMP. (C)	FIELD PR. (ATM)	VOL. WATER (CC)	CONTAINER PR. (ATM)	VOL. HDSP. (CC)	VOL. PSP. (CC)	He IN HDSP. UNCORR. (PPB)	He IN HDSP. CORR./DIL'N. (PPB)	He IN PSP. (PPB)
221	287.16	0.79	4.328	0.83	5.03	-0.03	5358.1	5476.2	93915.6
163	285.16	0.76	2.695	0.81	7.79	5.71	5032.0	4955.0	4568.0
193	292.16	0.76	0.314	0.78	5.77	5.53	5257.7	5265.5	5292.2
192	293.16	0.76	3.981	0.78	12.68	-0.38	4944.7	4824.7	20174.5
231	287.16	0.78	1.210	0.82	7.12	5.18	5343.3	5385.3	5584.6
242	290.16	0.77	0.696	0.80	8.40	4.70	5281.3	5297.1	5399.0
238	292.16	0.76	0.370	0.79	6.88	6.22	5254.8	5260.4	5283.1
189	283.16	0.78	1.098	0.84	9.41	5.59	5251.8	5255.7	5282.3
225	289.16	0.78	0.289	0.82	6.71	4.99	5260.7	5269.5	5309.3
240	289.16	0.78	0.921	0.81	6.88	5.12	5412.2	5484.0	5811.5
239A	291.16	0.76	0.438	0.79	4.76	7.14	5272.0	5285.4	5315.8
241	286.16	0.77	0.904	0.81	5.77	7.23	5326.1	5359.2	5454.4
224	289.16	0.79	2.312	0.82	7.79	5.01	5622.8	5921.9	6978.5
227	288.16	0.78	0.383	0.82	5.53	7.47	5240.0	5240.0	5240.0
06	302.16	0.78	0.197	0.79	5.60	6.60	5246.4	5249.0	5256.7
260	291.16	0.77	0.402	0.80	6.38	6.72	5272.0	5284.2	5326.2
191	293.16	0.76	0.352	0.78	8.74	7.56	5297.4	5315.0	5401.6
285	297.16	0.78	0.294	0.80	5.87	6.63	5240.0	5240.0	5240.0
230	285.16	0.77	0.658	0.82	6.54	7.76	5367.6	5456.8	5639.7
223	287.16	0.79	0.550	0.83	4.18	9.02	5316.6	5345.6	5394.7
202B	293.16	0.79	0.158	0.81	4.69	6.71	5272.0	5286.0	5318.2
194	293.16	0.76	0.257	0.79	7.05	5.35	5272.0	5284.9	5344.1
235	288.16	0.77	0.696	0.81	7.89	5.31	5447.3	5525.8	5950.5
229	285.16	0.77	0.907	0.82	9.48	4.52	5335.7	5369.9	5641.7
201	294.16	0.78	0.312	0.80	6.95	6.15	5240.0	5240.0	5240.0
232	286.16	0.77	0.576	0.81	6.44	6.76	5367.6	5415.9	5583.6
197	289.16	0.77	0.318	0.81	5.70	7.80	5240.0	5240.0	5240.0
233	284.16	0.77	0.435	0.82	7.29	6.61	5240.0	5240.0	5240.0
200	300.16	0.77	0.143	0.78	6.71	4.29	5240.0	5240.0	5240.0
199	293.16	0.76	0.301	0.79	5.77	7.13	5253.7	5259.0	5274.4
195	292.16	0.76	0.301	0.79	5.77	8.53	5240.0	5240.0	5240.0
254	283.16	0.77	0.736	0.82	7.79	5.41	5390.2	5447.1	5745.1
251	288.16	0.78	0.603	0.82	5.20	6.60	5253.7	5259.5	5274.9
196	290.16	0.77	0.344	0.80	6.27	6.73	5222.9	5216.3	5194.3
253	287.16	0.77	0.960	0.82	6.88	5.92	5376.6	5430.0	5650.6
198	293.16	0.78	0.286	0.80	5.94	6.16	5260.5	5269.0	5296.9
252B	293.16	0.79	1.138	0.82	6.44	6.76	5103.4	5051.7	4872.5
250	283.16	0.78	0.512	0.84	4.25	8.05	5212.7	5201.6	5181.4
245	286.16	0.78	0.375	0.82	5.53	6.27	5257.1	5264.3	5285.9
278	289.16	0.78	0.401	0.82	4.59	7.71	5216.1	5206.4	5186.4
****	0.00	0.00	0.000	0.00	0.00	0.00	0.0	0.0	0.0
255B	287.16	0.77	0.683	0.82	6.11	5.89	5376.6	5490.4	5749.7
247	284.16	0.78	0.458	0.83	5.26	7.94	5376.6	5428.3	5553.2
239B	291.16	0.76	0.483	0.79	4.76	7.54	5240.0	5240.0	5240.1
286	302.16	0.78	0.179	0.78	4.02	5.98	5274.1	5291.2	5325.5
205	294.16	0.78	0.312	0.81	6.11	7.59	5222.9	5216.7	5197.9
258	288.16	0.78	1.419	0.82	5.87	6.13	5461.2	5553.4	5853.0
252A	293.16	0.79	1.017	0.82	8.23	5.27	5103.4	5052.8	4761.2
259	293.16	0.76	1.157	0.79	4.86	5.44	5479.0	5595.0	5911.5
290	293.16	0.79	0.309	0.82	4.52	7.18	5258.2	5266.0	5282.4

249	284.16	0.79	0.629	0.84	6.38	6.82	5421.5	5490.3	5723.9
255A	287.16	0.77	0.878	0.82	7.56	4.74	5530.4	5648.4	6297.9
274	283.16	0.75	1.696	0.80	6.04	6.16	5167.4	5137.7	5037.8
256	286.16	0.77	1.025	0.82	6.27	5.93	5472.3	5567.5	5913.9
203	301.16	0.78	0.167	0.79	5.87	6.13	5276.3	5291.4	5340.7
267	284.16	0.75	2.165	0.80	7.45	3.65	5385.2	5450.6	5879.3
190A	293.16	0.79	0.301	0.81	6.95	5.85	5327.1	5361.1	5504.9
276	283.16	0.77	1.938	0.82	7.22	5.78	5385.2	5441.0	5691.5
277	288.16	0.78	0.491	0.82	5.36	6.34	5421.5	5499.1	5718.3
257	295.16	0.78	1.299	0.80	5.36	5.84	5294.4	5318.7	5391.0
270	288.16	0.76	1.228	0.80	9.48	4.02	5113.0	5066.0	4657.4
272	285.16	0.76	1.427	0.81	8.74	4.26	5348.9	5432.7	5826.4
275A	282.16	0.75	0.873	0.81	6.78	6.02	5367.0	5416.6	5615.3
275B	282.16	0.75	1.157	0.81	6.21	5.79	5330.7	5368.5	5506.0
269A	283.16	0.76	2.804	0.81	10.66	3.14	5283.6	5315.2	5568.6
204	297.16	0.78	1.700	0.80	5.43	5.57	5225.5	5218.9	5198.6
288	306.16	0.79	0.296	0.78	4.69	6.51	5247.3	5250.6	5258.1
246	285.16	0.78	0.620	0.83	5.70	6.70	5305.3	5331.6	5409.6
287B	291.16	0.78	3.454	0.82	10.15	-0.65	5185.6	5157.0	6513.0
279	285.16	0.76	1.001	0.81	6.11	5.29	5385.2	5448.9	5689.5
271	281.16	0.76	1.664	0.82	9.31	4.29	5167.4	5140.7	4926.3
280	285.16	0.75	1.781	0.80	7.22	4.78	5399.7	5466.2	5806.9
287A	291.16	0.78	3.378	0.82	10.15	-0.15	5240.0	5240.0	5213.9
282	283.16	0.75	1.729	0.80	8.63	4.37	5385.2	5496.9	6003.2
190B	293.16	0.79	0.281	0.81	6.27	4.23	5294.4	5320.3	5439.5
281	287.16	0.75	1.672	0.79	7.89	5.11	5367.0	5415.8	5687.0
268	288.16	0.75	2.041	0.79	5.77	5.23	5312.6	5345.6	5462.0
273	283.16	0.77	1.424	0.82	6.78	6.52	5414.2	5479.7	5728.6
265B	284.16	0.76	1.028	0.81	7.12	6.28	5385.2	5439.4	5665.0
283	290.16	0.79	0.243	0.82	5.70	7.30	5240.0	5240.0	5240.0
248	285.16	0.78	0.607	0.83	5.26	8.74	5428.7	5496.1	5650.3
289	293.16	0.79	0.358	0.81	5.53	5.27	5240.0	5240.0	5240.1
261	291.16	0.77	0.830	0.80	8.90	5.10	5399.7	5513.8	5991.5
262	288.16	0.76	0.280	0.80	6.27	7.73	5240.0	5240.0	5240.0
265A	284.16	0.76	1.138	0.81	6.88	7.02	5294.4	5314.0	5386.5
264	283.16	0.77	1.321	0.82	9.48	6.32	5290.8	5306.9	5407.1
266	284.16	0.76	1.656	0.81	8.63	6.57	5385.2	5433.0	5686.3
284	293.16	0.78	0.273	0.81	3.34	6.66	5240.0	5240.0	5240.0
263	290.16	0.77	0.536	0.81	9.07	5.43	5399.7	5454.8	5813.5
269B	283.16	0.76	3.184	0.81	8.97	5.03	5385.2	5437.1	5787.0
164	288.16	0.78	0.336	0.82	2.67	10.33	5253.7	5259.0	5263.9
182	303.16	0.78	0.262	0.78	3.51	8.69	5281.1	5297.9	5321.3
168	292.16	0.78	0.310	0.81	5.20	8.60	5226.3	5221.3	5210.1
177	293.16	0.78	0.590	0.80	7.22	7.48	5418.1	5478.7	5708.9
184	301.16	0.78	0.757	0.79	5.94	9.96	5377.0	5463.2	5596.1
176	293.16	0.78	0.332	0.81	5.87	6.63	5294.8	5316.7	5384.7
181	297.16	0.78	0.343	0.80	3.41	8.09	5283.8	5302.8	5329.3
175	285.16	0.77	0.648	0.81	7.05	8.25	5322.2	5349.1	5442.2
173	286.16	0.75	0.291	0.79	5.77	8.73	5253.7	5258.4	5270.6
174	287.16	0.76	0.995	0.80	6.88	7.82	5486.6	5570.5	5861.1

180	292.16	0.78	0.327	0.81	5.43	9.07	5267.4	5276.8	5298.9
172	285.16	0.77	1.096	0.82	8.74	7.26	5431.8	5491.7	5794.1
170	289.16	0.77	1.073	0.80	6.27	7.43	5377.0	5427.0	5584.9
186	301.16	0.78	0.476	0.79	4.59	7.81	5294.8	5316.9	5362.0
185	295.16	0.78	0.430	0.80	5.36	7.84	5240.0	5240.0	5240.0
179	294.16	0.78	0.603	0.81	5.60	5.90	5593.9	5747.8	6229.4
167	283.16	0.77	5.060	0.83	3.07	5.83	5226.3	5218.6	5208.0
154	297.16	0.78	0.219	0.79	4.02	7.78	5281.1	5298.5	5328.7
157B	285.16	0.78	11.244	0.83	3.75	0.25	5568.7	5979.6	13719.7
156	295.16	0.78	0.132	0.80	4.86	8.14	5308.5	5334.8	5391.4
149	295.16	0.78	0.210	0.80	2.16	9.84	5270.8	5283.6	5293.2
151	297.16	0.78	0.317	0.80	4.69	5.61	5270.8	5285.8	5324.0
147B	313.16	0.77	0.367	0.75	3.68	8.12	5286.2	5305.8	5335.4
145	302.16	0.79	1.163	0.79	4.52	5.98	5609.3	5785.2	6196.7
146	313.16	0.78	0.257	0.76	3.51	6.29	5270.8	5286.5	5312.4
171	289.16	0.77	0.848	0.81	5.60	9.40	5240.0	5240.0	5240.1
135	293.16	0.77	1.196	0.79	7.12	6.28	5455.4	5535.8	5870.4
143	303.16	0.78	0.265	0.78	4.42	6.78	5240.0	5240.0	5240.0
148	310.16	0.78	0.201	0.77	3.07	9.33	5289.2	5309.1	5331.8
144	287.16	0.78	9.225	0.82	3.51	-0.51	4932.2	4419.2	11200.7
142	296.16	0.78	0.407	0.80	2.57	9.03	5332.3	5372.1	5409.6
147A	313.16	0.77	0.359	0.75	3.17	7.33	5286.2	5308.2	5337.6
150	291.16	0.78	0.417	0.81	7.62	8.58	5270.8	5280.3	5316.2
141	288.16	0.78	0.320	0.82	2.73	7.27	5288.2	5312.3	5339.5
138	287.16	0.76	0.966	0.80	5.77	8.23	5368.5	5414.4	5536.6
139	290.16	0.76	0.311	0.80	2.84	9.16	5291.4	5312.8	5335.4
152	296.16	0.77	0.287	0.79	2.33	9.67	5286.2	5305.5	5321.2
183A	298.16	0.78	0.324	0.80	3.85	6.65	5270.8	5285.5	5311.8
183B	298.16	0.78	0.446	0.80	3.07	8.43	5301.6	5328.4	5360.6
178	301.16	0.78	0.339	0.79	3.51	6.49	5301.6	5332.4	5382.4
116	287.16	0.73	1.586	0.78	8.13	7.07	5392.4	5492.7	5782.7
133	285.16	0.76	0.881	0.81	6.54	9.76	5288.2	5303.0	5345.3
132	287.16	0.76	1.395	0.80	4.69	7.11	5336.4	5377.2	5467.8
130	287.16	0.77	0.965	0.81	7.62	7.48	5416.7	5475.2	5714.8
129	291.16	0.76	0.269	0.79	3.51	9.99	5400.7	5460.2	5537.6
126	287.16	0.77	0.503	0.81	8.30	8.50	5304.3	5323.4	5404.8
127	289.16	0.77	0.461	0.81	4.52	7.98	5448.9	5532.5	5698.1
124B	288.16	0.77	1.092	0.81	6.38	6.62	5481.0	5666.4	6076.3
124A	288.16	0.77	1.118	0.81	6.04	7.16	5341.6	5380.1	5498.2
123	290.16	0.77	0.680	0.80	3.85	8.15	5463.6	5556.8	5706.2
122	289.16	0.77	0.514	0.80	3.68	8.42	5358.6	5407.6	5480.8
121	290.16	0.77	0.918	0.80	5.20	6.80	5273.9	5288.0	5324.8
120	285.16	0.77	0.654	0.82	4.86	9.64	5395.8	5449.5	5555.1
117	286.16	0.74	1.417	0.78	5.36	9.64	5375.5	5465.8	5591.5
118	283.16	0.73	2.308	0.78	7.29	8.51	5307.8	5329.3	5405.6
137	287.16	0.75	1.226	0.80	6.27	6.93	5240.0	5240.0	5240.1
119	290.16	0.84	0.231	0.88	3.75	8.05	5206.1	5191.7	5169.3
136B	293.16	0.76	0.476	0.79	6.27	8.53	5400.7	5455.0	5613.2
131	285.16	0.76	0.867	0.81	7.39	7.51	5207.9	5197.1	5155.0
140	292.16	0.76	0.435	0.79	3.85	10.15	5256.1	5261.9	5270.2

114B	286.16	0.74	0.867	0.79	7.62	3.38	5477.1	5692.7	6712.3
112	283.16	0.73	1.551	0.78	7.89	7.81	5375.5	5418.7	5599.0
113	283.16	0.75	0.353	0.81	5.60	10.10	5189.2	5173.0	5135.9
108B	284.16	0.75	0.813	0.80	6.95	8.25	5382.3	5429.1	5588.3
110	287.16	0.73	1.016	0.78	6.88	11.12	5172.2	5153.4	5099.9
111	285.16	0.73	0.248	0.78	6.44	7.56	5206.1	5194.0	5154.8
109	283.16	0.74	0.992	0.79	9.24	6.96	5409.4	5514.0	5877.4
105	283.16	0.75	0.692	0.81	8.74	6.26	5240.0	5240.0	5240.1
106	287.16	0.75	0.533	0.79	6.61	7.59	5511.0	5606.4	5925.5
107	283.16	0.75	0.675	0.80	8.30	7.50	5358.6	5396.1	5568.7
108A	284.16	0.75	0.772	0.80	7.89	7.41	5409.4	5520.1	5818.4
103	283.16	0.76	0.838	0.81	7.29	8.01	5358.6	5397.4	5540.3
102	283.16	0.76	2.107	0.82	8.80	4.30	5612.6	5754.8	6804.9
104	283.16	0.76	0.741	0.81	5.77	7.13	5409.4	5475.1	5665.1
100A	288.16	0.76	0.479	0.80	7.39	6.91	5802.3	6195.5	7215.9
100B	288.16	0.76	0.545	0.80	6.61	7.59	5524.5	5724.9	6147.1
101	287.16	0.76	0.525	0.80	7.22	5.78	5331.5	5366.7	5524.8
115	283.16	0.74	2.146	0.79	7.45	7.25	5256.9	5262.6	5286.1
134	287.16	0.76	1.868	0.81	6.95	6.85	5443.3	5517.0	5797.4
114A	286.16	0.74	0.917	0.79	6.44	7.06	5578.8	5704.3	6127.7
214	283.16	0.79	4.242	0.84	4.25	4.95	5643.2	5862.3	6393.3
213	293.16	0.79	0.267	0.82	4.69	5.31	5240.0	5240.0	5240.0
211	285.16	0.78	2.448	0.83	7.79	4.51	5760.2	6183.1	7805.2
215A	287.16	0.79	0.322	0.83	3.75	7.35	5250.4	5255.1	5262.8
209	289.16	0.78	0.485	0.82	4.93	5.37	5310.2	5344.3	5439.9
136A	293.16	0.76	0.602	0.79	7.45	7.05	5312.8	5337.9	5441.5
157A	285.16	0.78	9.610	0.83	5.43	0.07	5344.0	5438.6	12304.5
165A	290.16	0.78	0.251	0.81	5.36	6.74	5214.0	5203.2	5174.0
207	296.16	0.78	0.164	0.80	3.75	7.35	5240.0	5240.0	5240.0
217	291.16	0.78	0.253	0.81	3.51	7.49	5234.1	5231.4	5227.4
218	287.16	0.79	0.747	0.83	5.77	6.53	5269.6	5281.6	5318.5
216	293.16	0.78	0.341	0.81	2.23	7.77	5240.0	5240.0	5240.0
208B	291.16	0.78	0.248	0.81	4.76	8.24	5228.2	5223.7	5214.3
208A	291.16	0.78	0.274	0.81	5.94	6.86	5210.4	5198.8	5163.3
210	291.16	0.78	0.440	0.82	2.33	8.97	5219.3	5210.1	5202.4
215B	287.16	0.79	0.365	0.83	4.59	7.21	5169.1	5139.1	5075.0
237	295.16	0.76	0.279	0.78	4.25	7.95	5228.2	5223.4	5214.5
220	293.16	0.79	0.515	0.81	5.26	6.94	5210.4	5198.3	5166.7
243	285.16	0.77	0.921	0.82	6.44	6.46	5372.9	5424.4	5608.3
236	289.16	0.76	0.611	0.80	4.25	7.45	5328.6	5404.3	5498.1
161	292.16	0.79	2.056	0.81	5.13	6.67	5083.9	5017.8	4847.7
158	285.16	0.78	5.365	0.83	7.52	5.98	5650.9	5803.1	6506.4
169B	293.16	0.78	0.486	0.80	7.02	6.38	5344.1	5382.9	5540.0
165B	290.16	0.78	0.293	0.81	5.26	7.94	5240.0	5240.0	5240.0
160	294.16	0.78	0.151	0.81	3.41	9.39	5292.0	5312.3	5338.6
159	296.16	0.79	0.177	0.80	4.42	9.38	5266.0	5275.4	5292.1
162	302.16	0.76	0.303	0.77	3.88	7.22	5292.0	5315.4	5356.0
188	299.16	0.78	0.442	0.79	3.48	8.22	5396.1	5462.8	5557.0
163	285.16	0.76	2.861	0.81	6.07	7.43	5031.9	4954.8	4722.8
166	296.16	0.78	0.232	0.79	5.40	7.70	5266.0	5275.9	5301.1

187	301.16	0.78	1.015	0.79	4.89	7.51	5448.1	5532.0	5722.1
125	285.16	0.77	1.503	0.82	6.44	8.06	5253.0	5257.5	5271.6
128	289.16	0.77	0.719	0.80	4.02	8.28	5500.2	5606.0	5783.3
169A	293.16	0.78	0.640	0.80	4.89	7.41	5370.1	5423.0	5543.8
154	293.16	0.78	0.262	0.81	2.87	8.63	5279.0	5296.0	5314.6
155	304.16	0.78	0.125	0.78	4.42	7.08	5240.0	5240.0	5240.0
219	287.16	0.79	1.049	0.83	3.64	8.06	5369.9	5425.4	5509.3
221	287.16	0.79	8.359	0.83	5.03	-0.03	5358.1	5476.2	28909.1
234	287.16	0.77	0.329	0.81	5.36	6.14	5402.4	5473.0	5676.6
222B	290.16	0.78	0.505	0.81	5.43	5.77	5269.6	5282.8	5323.2
228	290.16	0.78	0.551	0.81	6.71	6.59	5328.6	5361.9	5486.1
222A	291.16	0.78	0.386	0.82	6.88	5.52	5228.2	5223.4	5202.9

APPENDIX C

Data from the Fiji helium survey.

Pages C-3 through C-7 contain tables of sample locations in UTM's.

SAMPLE	LATITUDE	LONGITUDE
s124	1959.1570	666.3707
s362	1986.7289	652.4636
s360	1989.1711	653.9769
s359	1989.3389	656.5728
s358	1989.3433	658.0806
s353	1989.8564	661.5596
s350	1988.8467	663.5878
s351	1989.3186	663.1348
s352	1990.0950	662.8479
s349	1990.5806	663.4672
s348	1990.3713	664.1711
s366	1987.2415	662.3568
s326	1990.6455	666.8411
s115	1988.6719	670.5542
s341	1989.1467	670.4795
s342	1989.9233	670.5018
s339	1990.4661	670.3181
s340	1990.5137	671.1274
s187	1990.1230	673.1823
s375	1986.9585	669.0830
s376	1986.8811	668.0114
s377	1986.3442	667.1921
s378	1986.3743	666.4093
s379	1986.0601	665.7755
s380	1985.4583	664.7242
s381	1984.2815	666.0796
s382	1984.4414	667.0104
s387	1984.4622	667.8080
s191	1983.0889	669.8738
s389	1982.6387	667.5250
s390	1982.8010	666.4716
s391	1983.0088	665.6666
s394	1985.3760	658.5034
s395	1984.2170	658.3972
s396	1983.0854	658.5802
s397	1982.2273	659.4691
s398	1983.0615	660.4236
s399	1982.5505	661.7781
s400	1982.4326	662.9496
s401	1982.1836	663.9802
s392	1982.1763	665.1083
s404	1981.1750	667.3551
s393	1981.2502	665.8176
s402	1980.8201	666.1957

SAMPLE	LATITUDE	LONGITUDE
s403	1930.0708	665.6179
s405	1979.1885	665.9789
s208	1979.3262	670.0757
s121	1978.5710	669.9718
s119	1974.2595	672.2036
s118	1975.4832	671.1938
s412	1976.1450	670.2590
s117	1976.6824	667.4854
s444	1976.5813	665.3094
s445	1976.9504	659.2640
s446	1975.9678	660.4313
s449	1974.4348	662.3815
s450	1974.0652	662.9290
s440	1970.4026	664.8710
s441	1969.9075	664.3934
s120	1973.9019	670.6315
s217	1973.4565	670.9991
s220	1972.1260	670.1075
s219	1972.2317	669.0931
s434	1972.9488	667.4435
s222	1971.2866	667.4857
s227	1970.6067	667.6167
s233	1964.3584	670.7664
s442	1969.5586	665.4432
s458	1969.0110	665.6567
s443	1969.3799	664.8137
s441	1969.8975	664.3920
s465	1965.6226	662.5790
s466	1964.8262	663.1353
s467	1964.4529	663.7875
s478	1968.0010	661.6984
s234	1963.9349	667.5740
s328	1991.0435	664.5569
s325	1990.8662	665.8534
s305	1991.1047	670.1245
s184	1991.6770	673.7542
s303	1991.7598	669.8716
s304	1992.0270	670.4653
s344	1991.9639	668.5251
s311	1991.7693	666.7911
s324	1991.5830	665.5211
s321	1991.5874	664.9535
s318	1991.5132	662.8877
s263	1993.6094	658.6821

SAMPLE	LATITUDE	LONGITUDE
s265	1993.0698	660.8086
s266	1994.3208	660.6487
s267	1994.8850	661.3169
s261	1994.7854	662.1958
s291	1994.2747	662.7604
s314	1993.7810	661.9691
s319	1992.5769	662.7571
s292	1993.9216	663.2955
s320	1992.2358	663.8137
s322	1993.2080	664.2455
s323	1992.8267	664.8459
s313	1992.3582	665.5438
s312	1992.2666	666.0229
s294	1994.3093	664.5172
s280	1995.1587	665.0730
s295	1994.6660	666.5204
s307	1993.8035	666.7129
s310	1992.5884	666.9767
s301	1993.2317	669.1353
s306	1993.8804	668.8849
s288	1994.7612	668.4554
s296	1994.6931	667.5648
s287	1994.7356	669.5023
s284	1994.7781	670.2942
s300	1993.0872	670.0745
s299	1993.0872	671.0367
s298	1993.1975	671.9441
s283	1994.7273	671.0194
s282	1994.7383	671.6012
s170	1994.1904	673.1165
s179	1995.1797	674.2452
s168	1993.5222	677.0072
s171	1993.2344	677.4835
s162	1994.4231	677.9591
s155	1997.5371	677.6860
s205	1998.4946	676.4635
s206	1999.1780	676.0863
s207	1999.9331	675.8130
s499	1998.5605	675.9561
s498	1998.2476	675.0985
s497	1997.9548	674.4318
s496	1997.9866	673.8027
s169	1996.6978	674.5520
s493	1997.6978	674.5520

SAMPLE	LATITUDE	LONGITUDE
s492	1997.4856	671.4161
s491	1997.5156	671.1156
s285	1996.2324	670.4805
s286	1995.5906	670.3951
s272	1997.3591	669.1056
s273	1997.2639	668.2726
s275	1997.8433	667.1021
s277	1997.4534	667.4246
s270	1996.8931	667.6814
s289	1995.7993	668.2965
s297	1995.7070	667.2354
s269	1996.5144	667.0813
s268	1996.2000	666.4364
s278	1995.6062	665.8142
s274	1997.1768	666.2056
s248	1996.8005	661.3987
s250	1996.4463	662.9821
s251	1997.0298	663.6311
s252	1997.7327	664.1471
s253	1998.2754	663.6249
s254	1997.7588	664.8032
s255	1998.3694	664.3875
s256	1998.7825	664.9761
s257	1999.0171	665.9375
s258	1999.5525	665.0540
s259	2000.6162	664.8553
s260	2001.5437	664.0914
s114	2005.3916	655.5914
s135	2004.6821	656.2377
s136	2003.9460	655.6986
s137	2003.5276	657.4292
s138	2002.9133	658.8252
s129	2004.1323	661.7521
s130	2004.6396	661.7899
s131	2005.1475	661.4983
s132	2006.0515	661.0010
s133	2006.7339	661.4298
s134	2007.3179	661.7432
128s	2009.0435	661.0724
125s	2010.2000	660.4741
126s	2010.1238	660.9661
127s	2011.5757	660.9626
246s	1997.9797	661.1156
245s	1998.1614	661.4259

SAMPLE	LATITUDE	LONGITUDE
247s	1999.2490	660.5482
524s	2000.6436	661.4148
525s	2000.5286	662.1412
523s	2001.4497	662.3051
151s	2007.3838	668.7294
149s	2008.1692	667.8486
143s	2007.9661	666.1442
145s	2007.2412	664.8197
147s	2006.2119	663.9458
148s	2006.5911	663.0582
521s	2006.1963	661.9955
522s	2005.4558	662.9557
519s	2004.3745	665.0378
511s	2004.3577	667.2982
512s	2003.5762	668.0995
520s	2003.3450	666.4539
518s	2002.7878	665.1924
514s	2002.2334	664.9534
513s	2001.9465	667.9386
515s	2001.3804	666.7872
516s	2000.8152	667.9001
517s	1999.5464	667.0081
276s	1998.8457	666.7368
505s	1999.1990	668.1891
506s	2000.4050	669.0209
507s	2000.8547	670.1016
508s	2001.8318	669.5646
509s	2000.7136	671.3444
199s	1999.2585	672.9688
197s	2000.4622	674.8577
510s	2000.6301	673.7034

The following table presents the measured volumes of pore space and headspace for each sample, the amount of air added prior to analysis, the measured concentration of helium in the headspace, the estimated concentration of helium in headspace corrected for dilution and the difference (in ppb) between the two concentrations.

Sample No.	Soil Type	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air(cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
s124		3.5	4.7	3.0	5550	5816	266
s362	Loam	3.5	2.3	3.0	5480	5686	206
s360	Loam	3.5	2.5	3.0	5890	6447	557
s359	Loam	3.5	2.3	3.0	5970	6596	626
s358	Loam	3.5	4.4	3.0	5650	6001	351
s353	Loam	3.5	1.7	3.0	5650	6001	351
s350	Clay	3.5	3.2	3.0	5480	5686	206
s351	Clay	3.5	3.3	3.0	5730	6150	420
s352	Clay	3.5	1.9	3.0	5480	5686	206
s349	Loam	3.5	4.0	3.0	5570	5853	283
s348	Clay	3.5	3.2	3.0	5570	5853	283
s366	Loam	3.5	4.3	3.0	5680	6057	377
s326	Clay	3.5	3.0	3.0	5400	5537	137
s115		3.5	-0.8	3.0	5550	5816	266
s341	Clay	3.5	2.5	3.0	5890	6447	557
s342	Clay	3.5	3.2	3.0	5320	5389	69
s339	Clay	3.5	3.9	3.0	5650	6001	351
s340	Loam	3.5	2.2	3.0	5810	6299	489
s187	Sand	3.5	1.7	3.0	5470	5603	133
s375	Clay	3.5	2.3	3.0	5570	5853	283
s376	Clay	3.5	2.7	3.0	5740	6169	429
s377	Clay	3.5	2.7	3.0	5630	5964	334
s378	Loam	3.5	3.7	3.0	5410	5556	146
s379	Clay	3.5	2.4	3.0	5740	6169	429
s380	Clay	3.5	1.7	3.0	5410	5556	146
s381	Loam	3.5	3.2	3.0	5680	6057	377
s382	Clay	3.5	1.7	3.0	5900	6466	566
s387	Loam	3.5	3.2	3.0	5900	6466	566
		3.5	0.0	3.0	5600	5909	309
s191	Loam	3.5	3.7	3.0	5870	6410	540
s389	Loam	3.5	3.1	3.0	5680	6057	377
s390	Clay	3.5	3.0	3.0	5740	6169	429
s391	Clay	3.5	1.5	3.0	5570	5853	283
s394	Clay	3.5	1.8	3.0	5790	6261	471
s395	Clay	3.5	2.7	3.0	5520	5760	240
s396	Clay	3.5	-0.8	3.0	5850	6373	523
s397	Clay	3.5	1.3	3.0	5295	5342	47
s398	Clay	3.5	2.4	3.0	5520	5760	240
s399	Loam	3.5	3.7	3.0	5570	5853	283
s400	Clay	3.5	2.7	3.0	5740	6169	429

Sample No.	Soil Type	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air (cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
s401	Clay	3.5	3.0	3.0	5570	5853	283
s392	Clay	3.5	3.0	3.0	5630	5964	334
s404	Loam	3.5	4.4	3.0	5630	5964	334
s393	Loam	3.5	3.7	3.0	5740	6169	429
s402	Clay	3.5	2.9	3.0	5410	5556	146
s403	Clay	3.5	2.7	3.0	5680	6057	377
s405	Loam	3.5	4.6	3.0	5740	6169	429
s208		3.5	2.5	3.0	5700	6094	394
s121		3.5	3.8	3.0	5800	6280	480
s119	Clay	3.5	2.7	3.0	5600	5909	309
s118	Clay	3.5	4.3	3.0	5500	5723	223
s412	Loam	3.5	4.0	3.0	5740	6169	429
s117	Clay	3.5	4.7	3.0	5500	5723	223
s444	Clay	3.5	0.6	3.0	5730	6150	420
s445	Clay	3.5	2.2	3.0	5900	6466	566
s446	Clay	3.5	0.6	3.0	5570	5853	283
s449	Loam	3.5	5.5	3.0	5650	6001	351
s450	Clay	3.5	3.7	3.0	5320	5389	69
s440	Clay	3.5	3.5	3.0	5980	6614	634
s441	Clay	3.5	1.5	3.0	5730	6150	420
s120		3.5	3.8	3.0	5500	5723	223
s217		3.5	-0.7	3.0	5530	5779	249
s220	Loam	3.5	2.2	3.0	4840	4497	-343
s219		3.5	0.2	3.0	5410	5556	146
s434	Clay	3.5	3.0	3.0	5900	6466	566
s222	Clay	3.5	2.3	3.0	5820	6317	497
s227		3.5	-0.1	3.0	5410	5556	146
s233	Sand	3.5	4.2	3.0	5700	5878	178
s442	Clay	3.5	3.4	3.0	5730	6150	420
s458	Clay	3.5	0.8	3.0	6230	7079	849
s443	Clay	3.5	1.4	3.0	5730	6150	420
s441	Clay	3.5	1.5	3.0	5730	6150	420
s465	Clay	3.5	0.4	3.0	5570	5853	283
s466	Loam	3.5	4.2	3.0	5730	6150	420
s467	Loam	3.5	2.3	3.0	5900	6466	566
s478	Clay	3.5	3.1	3.0	5980	6614	634
s234	Sand	3.5	5.0	3.0	5760	5944	184
s323	Clay	3.5	3.9	3.0	5730	6150	420
s325	Loam	3.5	2.8	3.0	5810	6299	489
s305	Clay	3.5	2.4	3.0	5570	5853	283

Sample No.	Soil Type	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air(cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
s184		3.5	4.4	3.0	5700	6094	394
s303	Clay	3.5	3.6	3.0	5890	6447	557
s304	Clay	3.5	1.9	3.0	5650	6001	351
s344	Loam	3.5	4.5	3.0	5570	5853	283
s311	Clay	3.5	-0.0	3.0	5240	5240	0
s324	Clay	3.5	3.3	3.0	5240	5240	0
s321	Clay	3.5	2.3	3.0	5970	6596	626
s318	Clay	3.5	2.1	3.0	5570	5853	283
s263	Clay	3.5	-0.5	3.0	5480	5686	206
s265	Clay	3.5	2.3	3.0	5900	6466	566
s266	Clay	3.5	2.3	3.0	5240	5240	0
s267	Clay	3.5	1.4	3.0	5610	5927	317
s261	Clay	3.5	1.4	3.0	5610	5927	317
s291	Clay	3.5	2.1	3.0	5830	6336	506
s314	Loam	3.5	2.7	3.0	6050	6744	694
s319	Loam	3.5	2.9	3.0	5400	5537	137
s292	Loam	3.5	2.5	3.0	5680	6057	377
s320	Loam	3.5	4.1	3.0	5570	5853	283
s322	Loam	3.5	3.6	3.0	5730	6150	420
s323	Clay	3.5	1.6	3.0	5480	5686	206
s313	Clay	3.5	1.0	3.0	5890	6447	557
s312	Clay	3.5	3.8	3.0	5650	6001	351
s294	Clay	3.5	1.9	3.0	5240	5240	0
s280	Clay	3.5	2.5	3.0	5460	5649	189
s295	Clay	3.5	2.6	3.0	5530	5779	249
s307	Clay	3.5	2.6	3.0	5970	6596	626
s310	Clay	3.5	3.1	3.0	5650	6001	351
s301	Loam	3.5	2.9	3.0	5160	5091	-69
s306	Loam	3.5	3.1	3.0	5730	6150	420
s288	Clay	3.5	1.3	3.0	5750	6187	437
s296	Clay	3.5	2.7	3.0	5680	6057	377
s287	Loam	3.5	3.2	3.0	5610	5927	317
s284	Clay	3.5	3.2	3.0	5830	6336	506
s300	Loam	3.5	3.8	3.0	5530	5779	249
s299	Clay	3.5	0.9	3.0	5750	6187	437
s293	Clay	3.5	2.7	3.0	5530	5779	249
s283	Clay	3.5	1.8	3.0	5900	6466	566
s282	Clay	3.5	3.1	3.0	5680	6057	377
s170	Sand	3.5	-0.3	3.0	4890	4567	-323
s179	Clay	3.5	0.3	3.0	6220	7060	840
s168		3.5	1.4	3.0	6110	6856	746
s171	Sand	3.5	-0.7	3.0	5870	6546	676

Sample No.	Soil Type	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air(cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
s171	Sand	3.5	-0.7	3.0	5870	6546	676
s162	Sand	3.5	2.4	3.0	5700	5934	234
s155	Loam	3.5	1.7	3.0	6010	6670	660
s205	Sand	3.5	1.9	3.0	5530	5692	162
s206	Sand	3.5	5.7	3.0	5530	5625	95
s207	Sand	3.5	1.2	3.0	5640	5897	257
s499	Clay	3.5	2.7	3.0	5640	5983	343
s498	Clay	3.5	1.5	3.0	5328	5403	75
s497	Clay	3.5	1.2	3.0	5420	5574	154
s496	Clay	3.5	0.8	3.0	5370	5481	111
s169		3.5	1.3	3.0	5590	5890	300
s493	Clay	3.5	-0.6	3.0	5610	5927	317
s492	Clay	3.5	-0.2	3.0	5670	6039	369
s491	Clay	3.5	0.1	3.0	5910	6484	574
s285	Clay	3.5	2.3	3.0	5750	6187	437
s286	Clay	3.5	2.4	3.0	5680	6057	377
s272	Clay	3.5	1.0	3.0	5460	5649	189
s273	Clay	3.5	3.6	3.0	5830	6336	506
s275	Clay	3.5	3.2	3.0	5680	6057	377
s277	Loam	3.5	3.9	3.0	5680	6057	377
s270	Clay	3.5	2.7	3.0	5830	6336	506
s289	Loam	3.5	2.8	3.0	5610	5927	317
s297	Clay	3.5	4.4	3.0	5460	5649	189
s269	Clay	3.5	2.3	3.0	5830	6336	506
s268	Clay	3.5	2.4	3.0	5750	6187	437
s278	Loam	3.5	4.0	3.0	5680	6057	377
s274	Clay	3.5	2.3	3.0	5680	6057	377
s248	Loam	3.5	3.7	3.0	5660	6020	360
s250	Loam	3.5	3.6	3.0	5560	5834	274
s251	Clay	3.5	1.9	3.0	5720	6131	411
s252	Clay	3.5	21.9	3.0	5730	6150	420
s253	Clay	3.5	2.4	3.0	5450	5630	180
s254	Clay	3.5	2.2	3.0	5560	5834	274
s255	Clay	3.5	2.1	3.0	5820	6317	497
s256	Clay	3.5	2.7	3.0	5720	6131	411
s257	Clay	3.5	2.8	3.0	5450	5630	180
s258	Clay	3.5	1.2	3.0	5350	5444	94
s259	Clay	3.5	1.0	3.0	5660	6020	360
s260	Clay	3.5	2.3	3.0	5350	5444	94
s114	Clay	3.5	1.5	3.0	5550	5816	266
s135	Sand	3.5	1.9	3.0	5960	6359	399
s136	Clay	3.5	3.7	3.0	5860	6391	531
s137	Clay	3.5	2.3	3.0	5450	5630	180

Sample No.	Soil Type	Vol. hdsp. (cc)	Vol. psp. (cc)	Vol. added air(cc)	Meas. He (ppb)	Corr. He (ppb)	Diff.
s138	Sand	3.5	2.9	3.0	6110	6521	411
s129	Clay	3.5	3.1	3.0	5500	5723	223
s130	Clay	3.5	2.1	3.0	5190	5147	-43
s131		3.5	0.9	3.0	5500	5723	223
s132	Sand	3.5	1.7	3.0	5550	5728	178
s133	Sand	3.5	1.7	3.0	5650	5885	235
s134	Sand	3.5	1.3	3.0	5910	6329	419
128s	Sand	3.5	-0.2	3.0	5870	6448	578
125s	Sand	3.5	2.1	3.0	5830	6144	314
126s	Sand	3.5	4.2	3.0	5750	5948	198
127s	Sand	3.5	5.4	3.0	5550	5654	104
246s	Loam	3.5	2.6	3.0	5450	5630	180
245s	Loam	3.5	3.4	3.0	5240	5240	0
247s	Loam	3.5	2.9	3.0	5720	6131	411
524s	Clay	3.5	-0.2	3.0	5810	6299	489
525s	Clay	3.5	-0.6	3.0	5630	5964	334
523s	Clay	3.5	-0.3	3.0	5680	6057	377
151s	Sand	3.5	0.2	3.0	5450	5621	171
149s	Sand	3.5	0.6	3.0	6110	6739	629
143s	Sand	3.5	2.6	3.0	4930	4779	-151
145s	Sand	3.5	2.4	3.0	6010	6404	394
147s	Sand	3.5	2.2	3.0	6200	6706	506
148s	Sand	3.5	1.1	3.0	5550	5754	204
521s	Sand	3.5	-0.5	3.0	5680	6116	436
522s	Sand	3.5	-1.4	3.0	5680	6316	636
519s	Clay	3.5	1.1	3.0	5460	5649	189
511s	Clay	3.5	-0.3	3.0	5350	5444	94
512s	Clay	3.5	-0.1	3.0	5277	5309	32
520s	Clay	3.5	0.3	3.0	5900	6466	566
518s	Clay	3.5	0.3	3.0	5284	5322	38
514s	Sand	3.5	1.4	3.0	5570	5771	201
513s	Clay	3.5	3.7	3.0	5720	6131	411
515s	Clay	3.5	1.7	3.0	5180	5129	-51
516s	Clay	3.5	1.8	3.0	5720	6131	411
517s	Clay	3.5	1.5	3.0	5460	5649	189
276s	Loam	3.5	3.9	3.0	5240	5240	0
505s	Clay	3.5	1.1	3.0	5328	5403	75
506s	Clay	3.5	2.9	3.0	5500	5723	223
507s	Clay	3.5	1.5	3.0	5550	5816	266
508s	Clay	3.5	-0.8	3.0	5590	5890	300
509s	Clay	3.5	-1.4	3.0	5240	5240	0
199s	Loam	3.5	1.1	3.0	5590	5890	300

The following table contains data on the measured or estimated parameters for the Fiji Survey and report the calculated helium in pore space concentration for each sample.

SAMPLE NO.	SOIL TYPE	FIELD AIR TEMP.(C)	ASSUMED FIELD PR. (ATM.)	CONTAINER PR. (ATM.)	WT.DRY SOIL(g)	%TOTAL POROSITY (CALC.)	VOL. WATER (CC)	VOL.GAS PSP.(CC) (CALC.)	He/HDSP. UNCORR. (PPB)	He/HDSP. CORR./DIL'N (PPB)	He/PSP CALC. (PPB)
s124		30.6	1.0001	1.3012	7.16	70.0	1.60	4.70	5550	5816	6243
s362	Loam	27.8	0.9977	1.3101	10.96	54.0	2.60	2.26	5480	5686	6367
s360	Loam	25.6	0.9977	1.3198	10.96	54.0	2.40	2.46	5890	6447	8147
s359	Loam	25.6	0.9977	1.3198	9.46	60.3	3.10	2.33	5970	6596	8608
s358	Loam	25.6	0.9977	1.3198	8.76	63.3	1.30	4.39	5650	6001	6606
s353	Loam	30.6	0.9977	1.2981	10.76	54.9	3.20	1.74	5650	6001	7506
s350	Clay	31.1	0.9977	1.2957	7.76	67.5	2.90	3.17	5480	5686	6172
s351	Clay	33.9	0.9977	1.2840	6.56	72.5	3.20	3.32	5730	6150	7098
s352	Clay	31.1	0.9977	1.2957	7.86	67.0	4.10	1.93	5480	5686	6475
s349	Loam	33.3	0.9977	1.2863	6.86	71.2	2.40	4.01	5570	5853	6384
s348	Clay	32.8	0.9977	1.2887	8.86	62.8	2.50	3.16	5570	5853	6526
s366	Loam	27.2	0.9977	1.3125	7.06	70.4	2.00	4.33	5680	6057	6714
s326	Clay	28.3	0.9977	1.3077	6.66	72.1	3.50	2.99	5400	5537	5881
s115		30.6	1.0001	1.3012	9.26	61.2	6.30	-0.80	5550	5816	****
s341	Clay	31.7	0.9977	1.2934	8.96	62.4	3.10	2.52	5890	6447	8104
s342	Clay	32.2	0.9977	1.2910	9.06	62.0	2.40	3.18	5320	5389	5550
s339	Clay	31.7	0.9977	1.2934	8.56	64.1	1.90	3.87	5650	6001	6686
s340	Loam	31.1	0.9977	1.2957	10.56	55.7	2.80	2.21	5810	6299	7951
s187	Sand	30.6	1.0001	1.3012	11.46	51.9	3.00	1.67	5470	5603	6348
s375	Clay	34.4	0.9977	1.2817	9.16	61.6	3.20	2.34	5570	5853	6754
s376	Clay	32.2	0.9977	1.2910	7.06	70.4	3.60	2.73	5740	6169	7340
s377	Clay	31.1	0.9977	1.2957	7.46	68.7	3.50	2.68	5630	5964	6896
s378	Loam	31.7	0.9977	1.2934	6.36	73.3	2.90	3.70	5410	5556	5851
s379	Clay	32.2	0.9977	1.2910	9.16	61.6	3.10	2.44	5740	6169	7482
s380	Clay	31.7	0.9977	1.2934	7.56	68.3	4.40	1.75	5410	5556	6171
s381	Loam	27.8	0.9977	1.3101	7.76	67.5	2.90	3.17	5680	6057	6951
s382	Clay	30.6	0.9977	1.2981	9.76	59.1	3.60	1.72	5900	6466	8915
s387	Loam	33.3	0.9977	1.2863	8.26	65.4	2.70	3.18	5900	6466	7802
s191	Loam	30.6	1.0001	1.3012	8.06	66.2	2.30	3.66	5870	6410	7522
s389	Loam	34.4	0.9977	1.2817	9.36	60.7	2.40	3.07	5680	6057	6981
s390	Clay	34.4	0.9977	1.2817	9.36	60.7	2.50	2.97	5740	6169	7254
s391	Clay	32.2	0.9977	1.2910	7.76	67.5	4.60	1.47	5570	5853	7265
s394	Clay	32.2	0.9977	1.2910	9.76	59.1	3.50	1.82	5790	6261	8192
s395	Clay	32.2	0.9977	1.2910	9.76	59.1	2.60	2.72	5520	5760	6423
s396	Clay	32.2	0.9977	1.2910	10.56	55.7	5.80	-0.79	5850	6373	****
s397	Clay	31.1	0.9977	1.2957	10.56	55.7	3.70	1.31	5295	5342	5604
s398	Clay	34.4	0.9977	1.2817	10.06	57.8	2.80	2.40	5520	5760	6507
s399	Loam	31.1	0.9977	1.2957	6.16	74.2	3.00	3.67	5570	5853	6431
s400	Clay	31.1	0.9977	1.2957	7.76	67.5	3.40	2.67	5740	6169	7369
s401	Clay	31.1	0.9977	1.2957	7.06	70.4	3.30	3.03	5570	5853	6551
s392	Clay	27.8	0.9977	1.3101	8.76	63.3	2.70	2.99	5630	5964	6804
s404	Loam	26.7	0.9977	1.3149	7.76	67.5	1.70	4.37	5630	5964	6542
s393	Loam	27.8	0.9977	1.3101	8.86	62.8	2.00	3.66	5740	6169	7053
s402	Clay	30.0	0.9977	1.3005	7.46	68.7	3.30	2.88	5410	5556	5934
s403	Clay	30.0	0.9977	1.3005	11.66	51.1	1.90	2.70	5680	6057	7109

SAMPLE NO.	SOIL TYPE	FIELD AIR TEMP.(C)	ASSUMED FIELD PR. (ATM.)	CONTAINER PR. (ATM.)	WT.DRY SOIL(g)	%TOTAL POROSITY (CALC.)	VOL. WATER (CC)	VOL.GAS PSP.(CC) (CALC.)	He/HDSP. UNCORR. (PPB)	He/HDSP. CORR./DIL'N (PPB)	He/PSP CALC. (PPB)
s405	Loam	26.7	0.9977	1.3149	7.86	67.0	1.40	4.63	5740	6169	6868
s208		30.6	1.0001	1.3012	13.46	43.6	1.40	2.52	5700	6094	7274
s121		30.6	1.0001	1.3012	7.76	67.5	2.30	3.77	5800	6280	7239
s119	Clay	30.6	1.0001	1.3012	12.96	45.6	1.40	2.71	5600	5909	6768
s118	Clay	30.6	1.0001	1.3012	9.46	60.3	1.10	4.33	5500	5723	6112
s412	Loam	27.8	0.9977	1.3101	8.16	65.8	1.90	4.02	5740	6169	6973
s117	Clay	30.6	1.0001	1.3012	6.16	74.2	2.00	4.67	5500	5723	6083
s444	Clay	26.7	0.9977	1.3149	8.66	63.7	5.10	0.63	5730	6150	****
s445	Clay	30.0	0.9977	1.3005	7.96	66.6	3.80	2.20	5900	6466	8387
s446	Clay	30.0	0.9977	1.3005	7.96	66.6	5.40	0.60	5570	5853	****
s449	Loam	32.2	0.9977	1.2910	5.16	78.4	1.60	5.45	5650	6001	6488
s450	Clay	32.2	0.9977	1.2910	6.76	71.6	2.70	3.75	5320	5389	5525
s440	Clay	31.1	0.9977	1.2957	9.56	59.9	1.90	3.49	5980	6614	7984
s441	Clay	32.8	0.9977	1.2887	10.96	54.0	3.40	1.46	5730	6150	8276
s120		30.6	1.0001	1.3012	9.36	60.7	1.70	3.77	5500	5723	6169
s217		30.6	1.0001	1.3012	13.06	45.2	4.80	-0.73	5530	5779	****
s220	Loam	30.6	1.0001	1.3012	7.16	70.0	4.10	2.20	4840	4497	3333
s219		30.6	1.0001	1.3012	5.86	75.4	6.60	0.19	5410	5556	****
s434	Clay	33.9	0.9977	1.2840	7.16	70.0	3.30	3.00	5900	6466	7880
s222	Clay	30.6	1.0001	1.3012	11.76	50.7	2.30	2.26	5820	6317	7967
s227		30.6	1.0001	1.3012	9.96	58.2	5.30	-0.06	5410	5556	****
s233	Sand	30.6	1.0001	1.3012	10.76	54.9	0.70	4.24	5700	5878	6404
s442	Clay	30.6	0.9977	1.2981	8.86	62.8	2.30	3.36	5730	6150	7092
s458	Clay	32.2	0.9977	1.2910	11.86	50.3	3.70	0.82	6230	7079	****
s443	Clay	29.4	0.9977	1.3029	10.36	56.5	3.70	1.39	5730	6150	8384
s441	Clay	32.8	0.9977	1.2887	10.96	54.0	3.40	1.46	5730	6150	8276
s465	Clay	32.2	0.9977	1.2910	11.16	53.2	4.40	0.39	5570	5853	****
s466	Loam	31.1	0.9977	1.2957	8.46	64.5	1.60	4.21	5730	6150	6904
s467	Loam	30.6	0.9977	1.2981	11.96	49.8	2.20	2.29	5900	6466	8325
s478	Clay	31.1	0.9977	1.2957	9.76	59.1	2.20	3.12	5980	6614	8147
s234	Sand	30.6	1.0001	1.3012	7.16	70.0	1.30	5.00	5760	5944	6435
s328	Clay	30.6	0.9977	1.2981	6.86	71.2	2.50	3.91	5730	6150	6959
s325	Loam	30.6	0.9977	1.2981	10.06	57.8	2.40	2.80	5810	6299	7609
s305	Clay	37.8	0.9977	1.2679	7.26	69.5	3.90	2.36	5570	5853	6743
s184		30.6	1.0001	1.3012	8.36	64.9	1.40	4.44	5700	6094	6765
s303	Clay	34.4	0.9977	1.2817	7.76	67.5	2.50	3.57	5890	6447	7621
s304	Clay	36.1	0.9977	1.2748	6.56	72.5	4.60	1.92	5650	6001	7350
s344	Loam	34.4	0.9977	1.2817	7.16	70.0	1.80	4.50	5570	5853	6327
s311	Clay	32.8	0.9977	1.2887	11.96	49.8	4.50	-0.01	5240	5240	****
s324	Clay	32.2	0.9977	1.2910	7.86	67.0	2.70	3.33	5240	5240	5239
s321	Clay	32.2	0.9977	1.2910	7.26	69.5	4.00	2.26	5970	6596	8658
s318	Clay	31.1	0.9977	1.2957	8.66	63.7	3.60	2.13	5570	5853	6842
s263	Clay	34.4	0.9977	1.2817	12.26	48.6	4.90	-0.53	5480	5686	****
s265	Clay	31.1	0.9977	1.2957	9.26	61.2	3.20	2.30	5900	6466	8301
s266	Clay	30.0	0.9977	1.3005	7.16	70.0	4.00	2.30	5240	5240	5239

SAMPLE NO.	SOIL TYPE	FIELD AIR TEMP.(C)	ASSUMED FIELD PR. (ATM.)	CONTAINER PR. (ATM.)	WT.DRY SOIL(g)	%TOTAL POROSITY (CALC.)	VOL. WATER (CC)	VOL.GAS PSP.(CC) (CALC.)	He/HDSP. UNCORR. (PPB)	He/HDSP. CORR./DIL'N (PPB)	He/PSP CALC. (PPB)
s267	Clay	28.9	0.9977	1.3053	10.76	54.9	3.50	1.44	5610	5927	7560
s261	Clay	30.6	0.9977	1.2981	11.66	51.1	3.20	1.40	5610	5927	7608
s291	Clay	30.0	0.9977	1.3005	8.26	65.4	3.80	2.08	5830	6336	8145
s314	Loam	32.2	0.9977	1.2910	9.86	58.6	2.60	2.68	6050	6744	8691
s319	Loam	32.2	0.9977	1.2910	7.56	68.3	3.20	2.95	5400	5537	5885
s292	Loam	30.0	0.9977	1.3005	9.16	61.6	3.00	2.54	5680	6057	7169
s320	Loam	32.8	0.9977	1.2887	7.46	68.7	2.10	4.08	5570	5853	6375
s322	Loam	31.7	0.9977	1.2934	6.46	72.9	3.00	3.56	5730	6150	7036
s323	Clay	31.7	0.9977	1.2934	8.96	62.4	4.00	1.62	5480	5686	6625
s313	Clay	32.2	0.9977	1.2910	11.36	52.4	3.70	1.01	5890	6447	10476
s312	Clay	32.2	0.9977	1.2910	8.56	64.1	2.00	3.77	5650	6001	6704
s294	Clay	29.4	0.9977	1.3029	7.86	67.0	4.10	1.93	5240	5240	5238
s280	Clay	26.1	0.9977	1.3174	8.26	65.4	3.40	2.48	5460	5649	6217
s295	Clay	28.9	0.9977	1.3053	9.26	61.2	2.90	2.60	5530	5779	6494
s307	Clay	32.2	0.9977	1.2910	10.86	54.5	2.30	2.60	5970	6596	8404
s310	Clay	32.2	0.9977	1.2910	8.36	64.9	2.70	3.14	5650	6001	6841
s301	Loam	35.6	0.9977	1.2771	8.46	64.5	2.90	2.91	5160	5091	4912
s306	Loam	32.8	0.9977	1.2887	9.36	60.7	2.40	3.07	5730	6150	7180
s288	Clay	30.0	0.9977	1.3005	12.06	49.4	3.10	1.35	5750	6187	8592
s296	Clay	28.9	0.9977	1.3053	8.46	64.5	3.10	2.71	5680	6057	7102
s287	Loam	30.6	0.9977	1.2981	9.76	59.1	2.10	3.22	5610	5927	6670
s284	Clay	30.0	0.9977	1.3005	9.46	60.3	2.20	3.23	5830	6336	7515
s300	Loam	31.7	0.9977	1.2934	9.86	58.6	1.50	3.78	5530	5779	6275
s299	Clay	28.9	0.9977	1.3053	9.76	59.1	4.40	0.92	5750	6187	****
s298	Clay	31.1	0.9977	1.2957	8.16	65.8	3.20	2.72	5530	5779	6463
s283	Clay	31.1	0.9977	1.2957	11.96	49.8	2.70	1.79	5900	6466	8832
s282	Clay	31.1	0.9977	1.2957	8.36	64.9	2.70	3.14	5680	6057	6958
s170	Sand	30.6	1.0001	1.3012	11.26	52.8	5.00	-0.25	4890	4567	****
s179	Clay	30.6	1.0001	1.3012	12.36	48.2	4.00	0.33	6220	7060	****
s168		30.6	1.0001	1.3012	9.56	59.9	4.00	1.39	6110	6856	10809
s171	Sand	30.6	1.0001	1.3012	13.26	44.4	4.70	-0.70	5870	6546	****
s162	Sand	30.6	1.0001	1.3012	9.26	61.2	3.10	2.40	5700	5934	6930
s155	Loam	30.6	1.0001	1.3012	11.16	53.2	3.10	1.69	6010	6670	9583
s205	Sand	30.6	1.0001	1.3012	8.86	62.8	3.80	1.86	5530	5692	6528
s206	Sand	30.6	1.0001	1.3012	5.56	76.7	1.20	5.70	5530	5625	5860
s207	Sand	30.6	1.0001	1.3012	17.56	26.4	1.20	1.17	5640	5897	7838
s499	Clay	30.6	0.9977	1.2981	7.46	68.7	3.50	2.68	5640	5983	6938
s498	Clay	32.2	0.9977	1.2910	16.46	31.0	1.30	1.49	5328	5403	5784
s497	Clay	30.6	0.9977	1.2981	13.26	44.4	2.80	1.20	5420	5574	6530
s496	Clay	31.7	0.9977	1.2934	8.66	63.7	4.90	0.83	5370	5481	6440
s169		30.6	1.0001	1.3012	9.76	59.1	4.00	1.32	5590	5890	7567
s493	Clay	27.8	0.9977	1.3101	14.46	39.4	4.10	-0.56	5610	5927	****
s492	Clay	27.2	0.9977	1.3125	13.86	41.9	4.00	-0.23	5670	6039	****
s491	Clay	30.0	0.9977	1.3005	9.46	60.3	5.30	0.13	5910	6484	****
s285	Clay	30.6	0.9977	1.2981	12.36	48.2	2.00	2.33	5750	6187	7595
s286	Clay	30.0	0.9977	1.3005	11.86	50.3	2.10	2.42	5680	6057	7227
s272	Clay	28.9	0.9977	1.3053	3.96	83.4	6.50	1.00	5460	5649	6986
s273	Clay	27.8	0.9977	1.3101	10.06	57.8	1.60	3.60	5830	6336	7396
s275	Clay	28.3	0.9977	1.3077	11.16	53.2	1.60	3.19	5680	6057	6950

SAMPLE NO.	SOIL TYPE	FIELD AIR TEMP.(C)	ASSUMED FIELD PR. (ATM.)	CONTAINER PR. (ATM.)	WT.DRY SOIL(g)	%TOTAL POROSITY (CALC.)	VOL. WATER (CC)	VOL.GAS PSP.(CC) (CALC.)	He/HDSP. UNCORR. (PPB)	He/HDSP. CORR./DIL'N (PPB)	He/PSP CALC. (PPB)
s277	Loam	27.8	0.9977	1.3101	9.06	62.0	1.70	3.88	5680	6057	6791
s270	Clay	29.4	0.9977	1.3029	10.46	56.1	2.40	2.65	5830	6336	7769
s289	Loam	31.1	0.9977	1.2957	8.86	62.8	2.90	2.76	5610	5927	6790
s297	Clay	27.8	0.9977	1.3101	6.66	72.1	2.10	4.39	5460	5649	5973
s269	Clay	30.6	0.9977	1.2981	12.66	46.9	1.90	2.32	5830	6336	7974
s268	Clay	27.8	0.9977	1.3101	10.56	55.7	2.60	2.41	5750	6187	7546
s278	Loam	29.4	0.9977	1.3029	9.56	59.9	1.40	3.99	5680	6057	6771
s274	Clay	28.9	0.9977	1.3053	11.56	51.5	2.30	2.34	5680	6057	7269
s248	Loam	27.8	0.9977	1.3101	7.66	67.9	2.40	3.71	5660	6020	6751
s250	Loam	28.9	0.9977	1.3053	10.06	57.8	1.60	3.60	5560	5834	6409
s251	Clay	29.4	0.9977	1.3029	11.66	51.1	2.70	1.90	5720	6131	7752
s252	Clay	27.2	0.9977	1.3125	11.66	51.1	-17.30	21.90	5730	6150	6297
s253	Clay	28.9	0.9977	1.3053	12.46	47.7	1.90	2.40	5450	5630	6195
s254	Clay	28.9	0.9977	1.3053	10.16	57.4	3.00	2.16	5560	5834	6782
s255	Clay	30.0	0.9977	1.3005	10.26	57.0	3.00	2.13	5820	6317	8065
s256	Clay	30.0	0.9977	1.3005	10.26	57.0	2.40	2.73	5720	6131	7265
s257	Clay	30.0	0.9977	1.3005	11.36	52.4	1.90	2.81	5450	5630	6112
s258	Clay	31.7	0.9977	1.2934	9.86	58.6	4.10	1.18	5350	5444	6028
s259	Clay	31.1	0.9977	1.2957	13.06	45.2	3.10	0.97	5660	6020	****
s260	Clay	31.1	0.9977	1.2957	7.36	69.1	3.90	2.32	5350	5444	5746
s114	Clay	30.6	1.0001	1.3012	10.66	55.3	3.50	1.48	5550	5816	7148
s135	Sand	29.4	1.0001	1.3060	8.16	65.8	4.00	1.92	5960	6359	8357
s136	Clay	30.6	1.0001	1.3012	10.26	57.0	1.40	3.73	5860	6391	7468
s137	Clay	30.6	1.0001	1.3012	11.66	51.1	2.30	2.30	5450	5630	6217
s138	Sand	30.6	1.0001	1.3012	8.86	62.8	2.80	2.86	6110	6521	8075
s129	Clay	30.6	1.0001	1.3012	12.66	46.9	1.10	3.12	5500	5723	6262
s130	Clay	30.6	1.0001	1.3012	9.26	61.2	3.40	2.10	5190	5147	4994
s131		30.6	1.0001	1.3012	13.76	42.3	2.90	0.91	5500	5723	****
s132	Sand	30.6	1.0001	1.3012	14.76	38.1	1.70	1.73	5550	5728	6705
s133	Sand	30.6	1.0001	1.3012	14.76	38.1	1.70	1.73	5650	5885	7178
s134	Sand	30.6	1.0001	1.3012	16.96	28.9	1.30	1.30	5910	6329	9234
128s	Sand	30.6	1.0001	1.3012	13.86	41.9	4.00	-0.23	5870	6448	****
125s	Sand	26.7	1.0001	1.3181	13.66	42.7	1.70	2.14	5830	6144	7607
126s	Sand	30.6	1.0001	1.3012	10.26	57.0	0.90	4.23	5750	5948	6533
127s	Sand	30.6	1.0001	1.3012	8.46	64.5	0.40	5.41	5550	5654	5922
246s	Loam	26.7	0.9977	1.3149	10.06	57.8	2.60	2.60	5450	5630	6149
245s	Loam	29.4	0.9977	1.3029	9.16	61.6	2.10	3.44	5240	5240	5240
247s	Loam	29.4	0.9977	1.3029	9.46	60.3	2.50	2.93	5720	6131	7187
524s	Clay	32.2	0.9977	1.2910	14.96	37.3	3.60	-0.25	5810	6299	****
525s	Clay	32.2	0.9977	1.2910	12.86	46.1	4.70	-0.55	5630	5964	****
523s	Clay	32.2	0.9977	1.2910	10.86	54.5	5.20	-0.30	5680	6057	****
151s	Sand	30.6	1.0001	1.3012	12.76	46.5	4.00	0.18	5450	5621	****
149s	Sand	30.6	1.0001	1.3012	11.26	52.8	4.10	0.65	6110	6739	****
143s	Sand	30.6	1.0001	1.3012	14.46	39.4	0.90	2.64	4930	4779	4169

SAMPLE NO.	SOIL TYPE	FIELD AIR TEMP.(C)	ASSUMED FIELD PR. (ATM.)	CONTAINER PR. (ATM.)	WT.DRY SOIL(g)	%TOTAL POROSITY (CALC.)	VOL. WATER (CC)	VOL.GAS PSP.(CC) (CALC.)	He/HDSP. UNCORR. (PPB)	He/HDSP. CORR./DIL'N (PPB)	He/PSP CALC. (PPB)
145s	Sand	30.6	1.0001	1.3012	10.16	57.4	2.80	2.36	6010	6404	8106
147s	Sand	30.6	1.0001	1.3012	15.66	34.3	0.90	2.19	6200	6706	9040
148s	Sand	30.6	1.0001	1.3012	12.56	47.3	3.20	1.06	5550	5754	7402
521s	Sand	31.1	0.9977	1.2957	13.96	41.5	4.20	-0.47	5680	6116	****
522s	Sand	31.1	0.9977	1.2957	16.76	29.7	4.10	-1.43	5680	6316	****
519s	Clay	30.0	0.9977	1.3005	9.46	60.3	4.30	1.13	5460	5649	6868
511s	Clay	28.9	0.9977	1.3053	11.46	51.9	5.00	-0.33	5350	5444	****
512s	Clay	30.0	0.9977	1.3005	11.66	51.1	4.70	-0.10	5277	5309	****
520s	Clay	30.6	0.9977	1.2981	11.26	52.8	4.40	0.35	5900	6466	****
518s	Clay	30.0	0.9977	1.3005	13.06	45.2	3.80	0.27	5284	5322	6200
514s	Sand	30.6	0.9977	1.2981	13.16	44.8	2.60	1.43	5570	5771	7043
513s	Clay	30.6	0.9977	1.2981	7.16	70.0	2.60	3.70	5720	6131	6969
515s	Clay	30.0	0.9977	1.3005	10.66	55.3	3.30	1.68	5180	5129	4899
516s	Clay	29.4	0.9977	1.3029	13.36	44.0	2.20	1.76	5720	6131	7885
517s	Clay	30.0	0.9977	1.3005	13.76	42.3	2.30	1.51	5460	5649	6583
276s	Loam	28.9	0.9977	1.3053	10.96	54.0	1.00	3.86	5240	5240	5240
505s	Clay	31.7	0.9977	1.2934	10.06	57.8	4.10	1.10	5328	5403	5900
506s	Clay	35.6	0.9977	1.2771	13.56	43.1	1.00	2.88	5500	5723	6307
507s	Clay	30.0	0.9977	1.3005	9.76	59.1	3.80	1.52	5550	5816	7112
508s	Clay	27.8	0.9977	1.3101	10.36	56.5	5.90	-0.81	5590	5890	****
509s	Clay	29.4	0.9977	1.3029	9.96	58.2	6.60	-1.36	5240	5240	****
199s	Loam	30.6	1.0001	1.3012	12.56	47.3	3.20	1.06	5590	5890	7975
197s	Sand	30.6	1.0001	1.3012	11.66	51.1	2.70	1.90	5240	5240	5239
510s	Clay	30.0	0.9977	1.3005	5.96	75.0	6.40	0.35	5328	5403	6800