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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

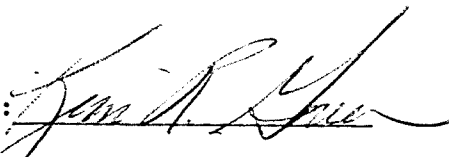
Kim R. Green


T-2841

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Golden, Colorado

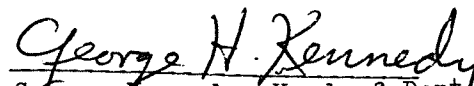
Date 5/2/84, 1984

Signed: 
Kim R. Green

Approved: 
Ron Klusman, Thesis Advisor

Golden, Colorado

Date 5/2/84, 1984


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 uncertainty 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

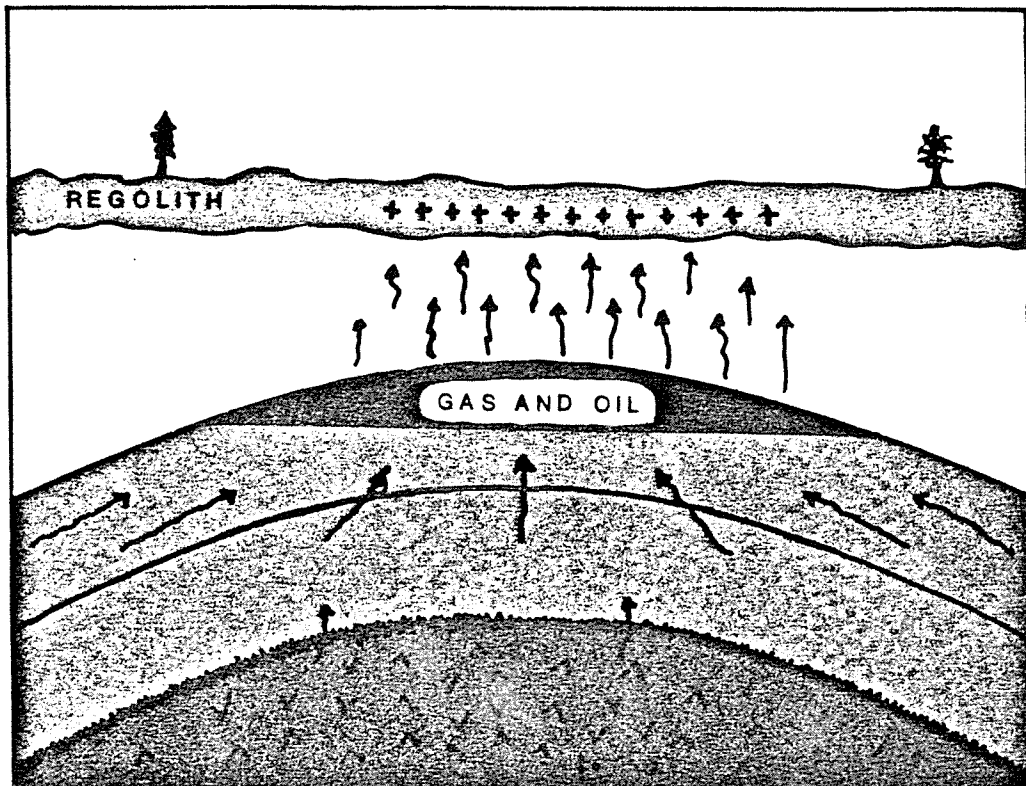


Figure 1. Apical type high helium anomaly produced in soils over a petroleum deposit.

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 relatively 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 algorithms 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.

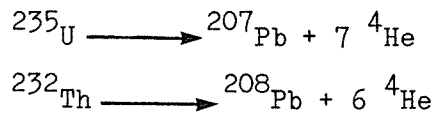
A second field study was conducted over the Long Valley caldera, near Mammoth Lakes California in order to facilitate the development of algorithms for determining actual concentrations of helium in soils, and the identification of associated parameters. This area has been undergoing unusual seismic 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, ^3He and ^4He .

It is probable that some primordial helium (^3He and ^4He) 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, ^4He atoms. This decay scheme is shown in figure 2. In addition to the uranium-238 series, ^4He can also be generated in the decay series of uranium-235 and thorium-232. The decay of these can be summarized as:



(Moore and Esfandiari, 1971).

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

The radiogenic decay of tritium generated in the crust (from ^7Li and ^6Li) and the atmosphere (from ^{14}N) represent an additional source of the ^3He isotope (Morrison and Pine, 1955). The production of ^3He is much lower than the production of ^4He . Its natural abundance is only 10^{-6} of the abundance ^4He (Mamyrin, et al., 1970). While the ratio of $^3\text{He}/^4\text{He}$ 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 ^4He in the remainder of this

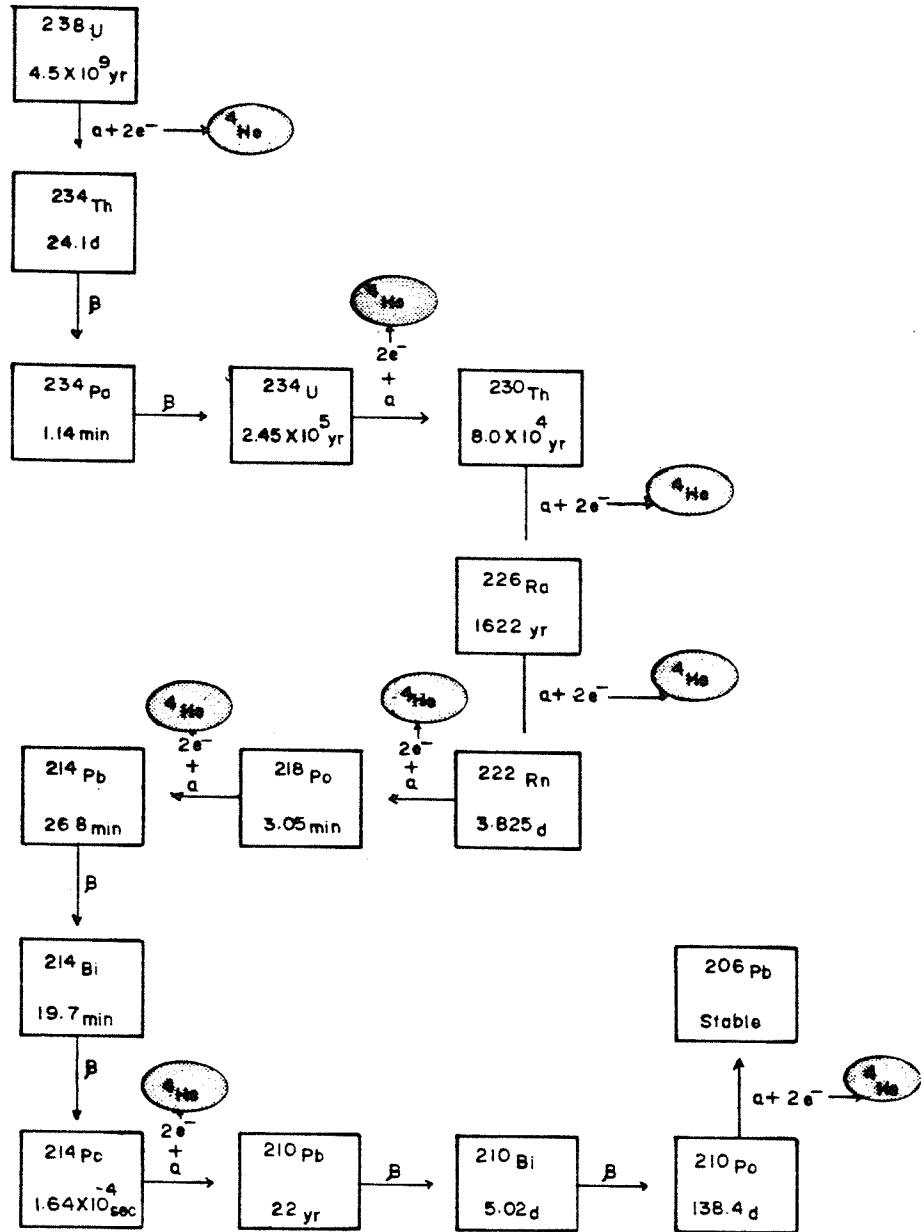


Figure 2. Decay scheme for ^{238}U , showing type of decay, decay products, half lives, and production of helium-4 (after Rose, Hawkes, and Webb, 1979).

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 \AA (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 sedimentary 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 microfractures 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 disseminated 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

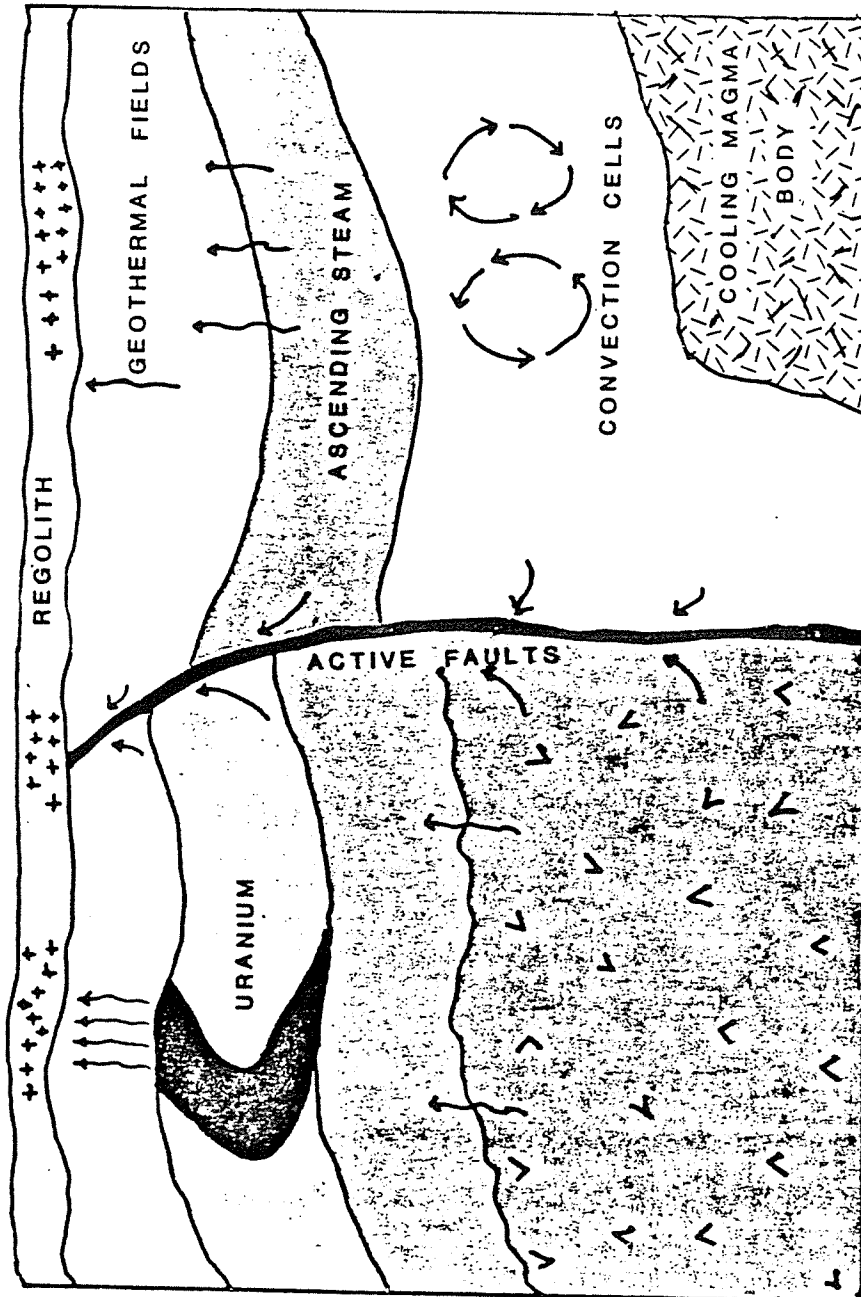


Figure 3. Possible origins for anomalously high helium concentrations in near-surface soils (after Clark, 1981).

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 fluctuations 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 elliptical 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

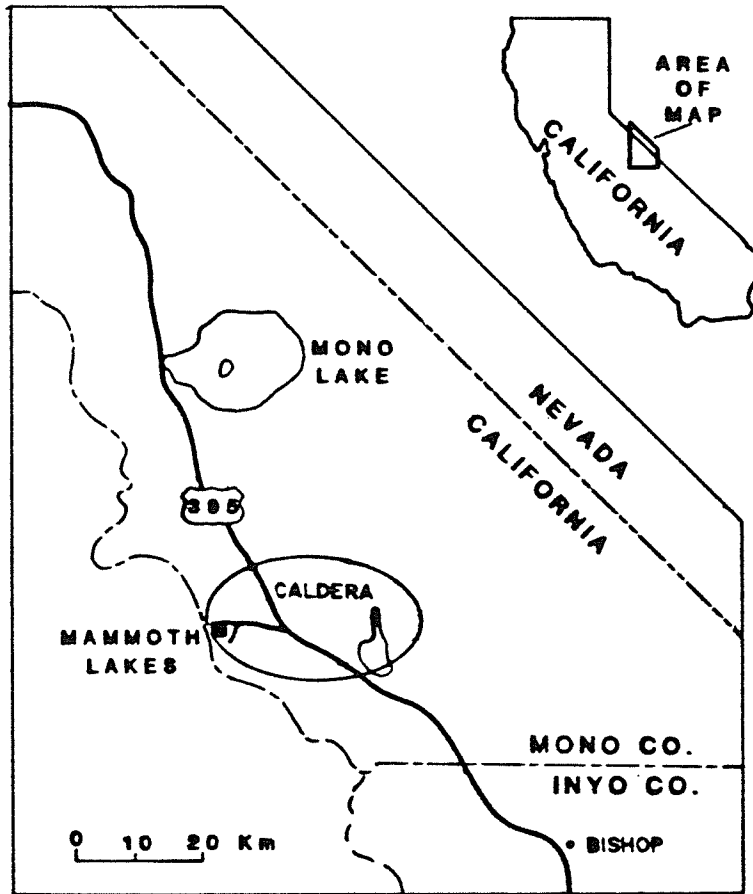


Figure 4. Location map of the Long Valley caldera (after Sorey et al., 1978).

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 algorithm 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 sealant 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°C . Instantaneous pressure readings were taken to the nearest 0.1 inches (of Hg) using an aneroid barometer.

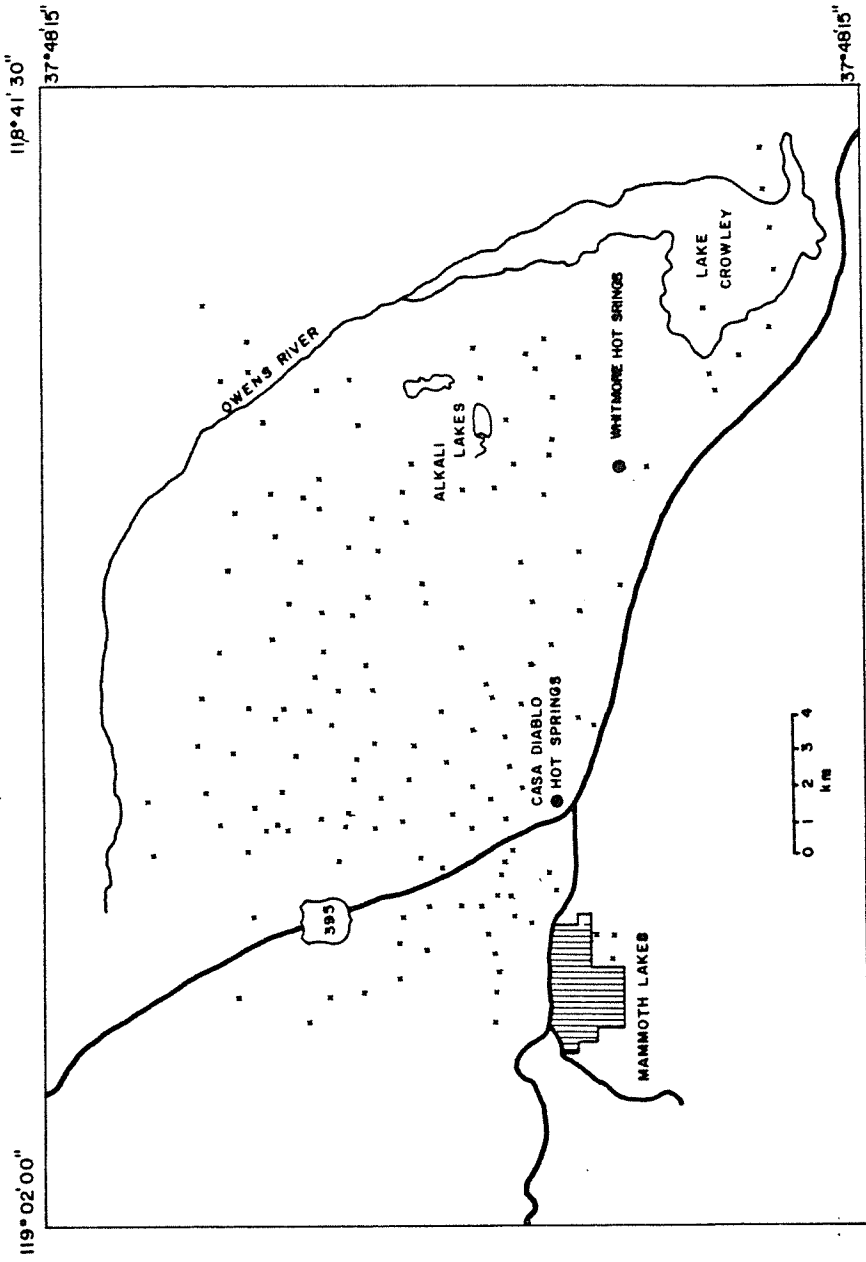


Figure 5. Sample location map for the Long Valley Survey.

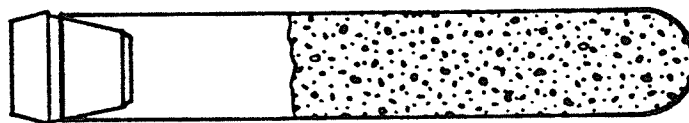


Figure 6. Vacutainer brand blood specimen tube used for soil sample collection.

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

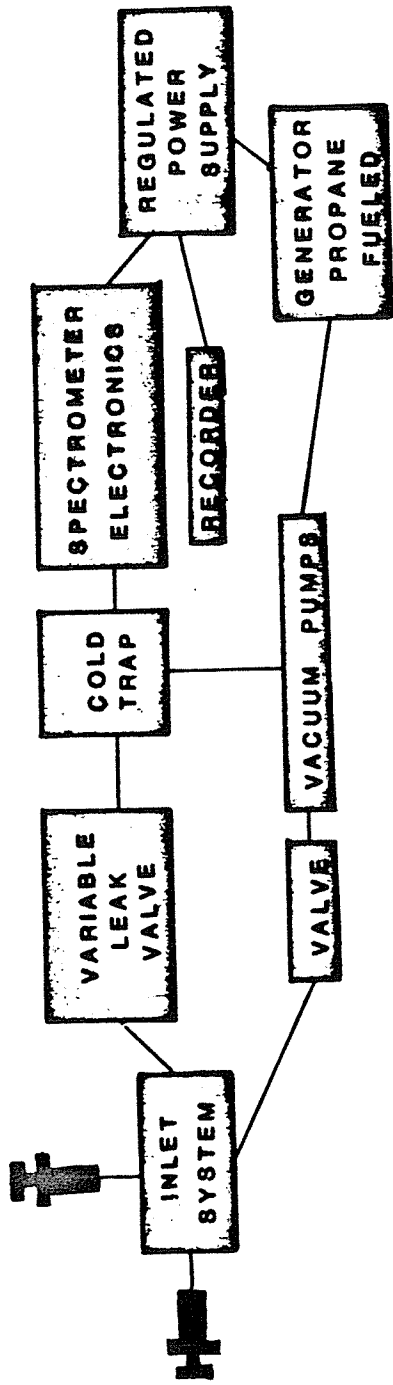


Figure 7. Generalized diagram of mass spectrometer used for helium detection (after Reimer, 1976).

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°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°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:

$$\frac{T_1 P_f}{T_f} = P_c$$

where

T_1 = 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 concentrations in soils are generally

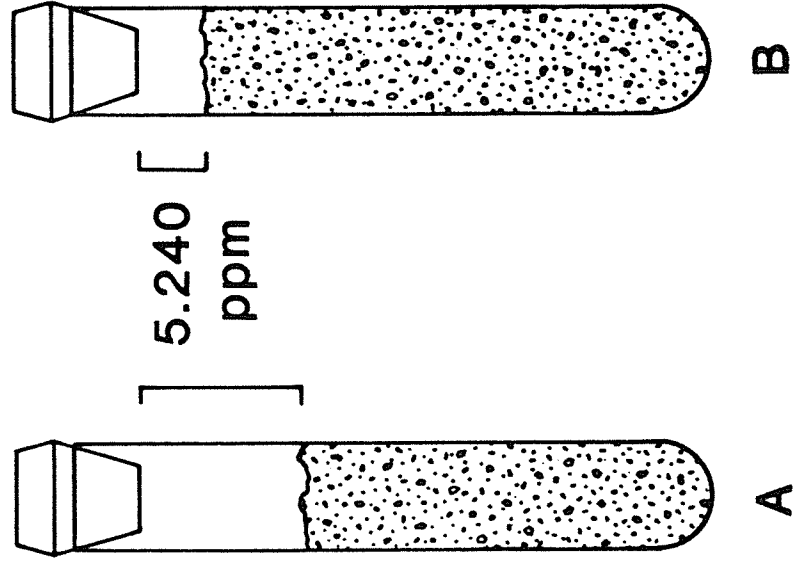


Figure 8. Contained soil samples, illustrating the effect of atmospheric dilution.

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 volumes of 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.

Helium in Soils

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 occurred:

$$\text{He}_{\text{initial}} = \text{He}_{\text{final}} \quad (1)$$

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:

$$\text{He}_{\text{Initial}} = I_p + I_w + I_h \quad (2)$$

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:

$$\text{He}_{\text{final}} = F_p + F_w + F_h \quad (3)$$

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:

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

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

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

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:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (\text{constant number of moles, ideal gas}) \quad (6)$$

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:

$$\begin{aligned} I_h &= V_{hc} \times 1\text{mole}/22.4 \text{ l} \\ \text{or} \quad I_h &= V_{hc} \times 1\text{mole}/22414\text{cc} \end{aligned} \quad (7)$$

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:

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

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

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

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:

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

where

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

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

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

Rearranging (10):

$$V_{hc} = \frac{V_{hf} P_f 273.16^\circ K}{T_f \cdot \text{latm}} \quad (11)$$

Substituting (9) into (11):

$$V_{hc} = \frac{\left(\frac{5.240 \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \right) \cdot P_f 273.16^\circ K}{T_f \cdot \text{latm}} \quad (12)$$

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:

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

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:

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

where Y is the number of cc's of helium in 10^6 cc'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)):

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

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:

$$\frac{P_c V_{hl}}{T_1} = \frac{1 \text{ atm } V_{fc}}{273.16^\circ \text{K}} \quad (16)$$

where

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

T_1 = temperature of sample at time of analysis (lab, in $^\circ\text{K}$)

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):

$$V_{fc} = \frac{V_{hl} \cdot P_c \cdot 273.16^\circ \text{K}}{T_1 \cdot 1 \text{ atm}} \quad (17)$$

Substituting (14) into (16):

$$V_{fc} = \frac{\left(\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \right) P_c \cdot 273.16^\circ\text{K}}{T_1 \cdot \text{latm}} \quad (18)$$

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:

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

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

$$F_h = \frac{\left(\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \right) \cdot P_c \cdot 273.16^\circ\text{K} \cdot 1 \text{ mol}}{T_1 \cdot \text{latm} \cdot 22414 \text{ cc}} \quad (20)$$

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

Calculation of F_p . 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:

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

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:

$$\frac{P_c V_{pl}}{T_1} = \frac{1 \text{ atm } V_{pc}}{273.16^\circ \text{K}} \quad (22)$$

where

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

Rearranging (22):

$$V_{pc} = \frac{V_{pl} P_c 273.16^\circ \text{K}}{T_1 \cdot 1 \text{ atm}} \quad (23)$$

Substituting (21) into (23)

$$V_{pc} = \frac{\left(\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot V_p \right) \cdot P_c \cdot 273.16^\circ \text{K}}{T_1 \cdot 1 \text{ atm}} \quad (24)$$

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:

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

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

$$F_p = \frac{\left(\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot V_p \cdot P_c \cdot 273.16^\circ \text{K} \right)}{T_1 \cdot 1 \text{ atm}} \cdot \frac{1 \text{ mole}}{22414 \text{ cc}} \quad (26)$$

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 equilibrium partial vapor pressure of that gas:

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

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 4.5×10^{-8} cc He/g H_2O at $35^\circ C$ 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:

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

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

${}^1K_{\text{He}}$ = 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:

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

where

X_i = the mole fraction of i , in the mixture

P = the total pressure of the mixture

Therefore,

$$P_{\text{He}} = \varepsilon X_{\text{He}} \cdot P_c \quad (30)$$

where

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

$\varepsilon X_{\text{He}}$ = 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:

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

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:

$$x_{\text{He}} = \frac{n_{\text{He}}}{(n_{\text{air}} + n_{\text{He}})} \quad (32)$$

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} :

$$n_{\text{He}} \ll n_{\text{air}} \quad (33)$$

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:

$$g_{x_{\text{He}}} = \frac{n_{\text{He in air}}}{n_{\text{air}}} \quad (34)$$

Instead of the mole fraction, $g_{x_{\text{He}}}$, a volume fraction can be used by observing the following relationships:

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

(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, $g_{x_{\text{He}}}$, then becomes:

$$g_{X_{\text{He}}} = \frac{n_{\text{He}}}{n_{\text{air}}} = \frac{\frac{P_c V_{\text{He}}}{RT_1}}{\frac{P_c V_{\text{air}}}{RT_1}} \quad (36)$$

Cancellation of equivalent terms in (36) yields:

$$g_{X_{\text{He}}} = \frac{n_{\text{He}}}{n_{\text{air}}} = \frac{V_{\text{He}}}{V_{\text{air}}} \quad (37)$$

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

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

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

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

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

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

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:

$$X_{\text{He}} = \frac{P_{\text{He}}}{l_{\text{K}_{\text{He}}}} \quad (41)$$

Substituting equation (40) into (41):

$$X_{\text{He}} = \frac{[Y]_{\text{cc He}}}{10^6 \text{ cc air}} \cdot P_c \cdot \frac{1}{l_{\text{K}_{\text{He}}}} \quad (42)$$

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:

$$X_{\text{He}} = \frac{n_{\text{He in H}_2\text{O}}}{n_{\text{tot}}} \quad (43)$$

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/ccH₂O), therefore, the moles of helium present in the water of a sample is very small relative to the number of moles of H₂O:

$$n_{\text{He}} \ll n_{\text{H}_2\text{O}} \quad (44)$$

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

$$X_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{H}_2\text{O}}} \quad (45)$$

where

$$n_{\text{H}_2\text{O}} = \text{moles of soil moisture (water) present in soil}$$

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

$$n_{\text{He}} = \frac{\frac{[\text{Y}]_{\text{cc He}}}{10^6 \text{ cc air}} \cdot P_c}{1_{K_{\text{He}}}} \cdot n_{\text{H}_2\text{O}} \quad (46)$$

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:

$$n_{\text{He}} = F_w \quad (47)$$

Substituting (47) into (46):

$$F_w = \frac{\frac{[\text{Y}]_{\text{cc He}}}{10^6 \text{ cc air}} \cdot P_c}{1_{K_{\text{He}}}} \cdot n_{\text{H}_2\text{O}} \quad (48)$$

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:

$$n_{\text{H}_2\text{O}} = \frac{(1.0 \text{ g/cc} \cdot V_w)}{18.01 \text{ g/mol}} \quad (49)$$

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:

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

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):

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

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:

$$\begin{aligned}
 I_p + I_w = & \left[\frac{\left(\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot V_p \right) \cdot P_c \cdot 273.16^\circ\text{K}}{T_1 \cdot \text{latm}} \cdot \frac{1 \text{ mole}}{22414 \text{ cc}} \right] \\
 + & \left[\frac{\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot P_c}{l_{K_{\text{He}}}} \cdot \frac{(1.0 \text{ g/cc} \cdot V_w)}{18.01 \text{ g/mol}} \right] \\
 + & \left[\frac{\left(\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \right) \cdot P_c \cdot 273.16^\circ\text{K}}{T_1 \cdot \text{latm}} \cdot \frac{1 \text{ mol}}{22414 \text{ cc}} \right] \\
 - & \left[\frac{\frac{5.240 \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \cdot P_f \cdot 273.16^\circ\text{K}}{T_f \cdot \text{latm}} \cdot \frac{1 \text{ mol}}{22414 \text{ cc}} \right] \quad (51)
 \end{aligned}$$

Equation (51) can be somewhat simplified. Combining the terms for

F_h , F_p , and I_h and rearranging yields:

$$\begin{aligned}
 I_p + I_w = & \frac{273.16^\circ\text{K} \cdot 1 \text{ mole}}{22414 \text{ cc} \cdot \text{latm}} \left[\frac{[Y] \text{ cc He} \cdot P_c}{10^6 \text{ cc air}} \cdot (V_h + V_p) \right] \\
 - & \left[\frac{5.240 \text{ cc He} \cdot V_h \cdot P_f}{10^6 \text{ cc air} \cdot T_f} \right] \\
 + & \left[\frac{\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot P_c}{l_{K_{\text{He}}}} \cdot \frac{(1.0 \text{ g/cc} \cdot V_w)}{18.01 \text{ g/mol}} \right] \quad (52)
 \end{aligned}$$

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 equilibrium, 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:

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

For helium present in gaseous pore space, this becomes:

$$P_{He} V_p = n_p RT_f \quad (54)$$

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 $^{\circ}$ K) or 82.05 cc atm per (mole $^{\circ}$ K)

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

T_f = temperature in field at time of collection in $^{\circ}$ 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 porespace is symbolized as:

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

Substitution of (55) into (54) yields:

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

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

$$P_{He} = X_{He} f_{K_{He}} \quad (57)$$

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:

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

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:

$$P_{He} = \frac{n_w f_{K_{He}}}{n_{H_2O}} \quad (59)$$

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

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

Substituting (60) into (59):

$$P_{He} = \frac{I_w}{n_{H_2O}} \cdot f_{K_{He}} \quad (61)$$

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

$$P_{He} = \frac{\frac{I_w}{1.0g/cc \cdot V_w}}{18.01g/mol} \cdot f_{K_{He}} \quad (62)$$

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):

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

Setting (63) equal to (62) yields:

$$\frac{I_p RT_f}{V_p} = \frac{\frac{I_w}{1.0g/cc \cdot V_w}}{18.01g/mol} \cdot f_{K_{He}} \quad (64)$$

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):

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

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

$$\frac{I_p RT_f}{V_p} = \frac{(S - I_p)}{1.0g/cc \cdot V_w} \cdot f_{K_{He}} \quad (68)$$

18.01g/mol

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:

$$\frac{I_p \cdot RT_f}{V_p} = \frac{f_{K_{He}} \cdot S}{1.0g/cc \cdot V_w} - \frac{f_{K_{He}} I_p}{1.0g/cc V_w} \quad (69)$$

18.01g/mol

$$\frac{I_p \cdot R \cdot T_f}{V_p} + \frac{f_{K_{He}} I_p}{1.0g/cc \cdot V_w} = \frac{f_{K_{He}} \cdot S}{1.0g/cc \cdot V_w} \quad (70)$$

18.01g/mol

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

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

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

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

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:

$$\begin{aligned}
 I_p = & \frac{f_{K_{He}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}} \cdot \left[\frac{273.16^\circ \text{K} \frac{1 \text{ mol}}{22414 \text{ cc}}}{1 \text{ atm}} \cdot \right. \\
 & \left. \left[\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot P_c \right. \right. \\
 & \left. \left. \frac{(V_h + V_p)}{T_1} - \frac{5.240 \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \cdot P_f \right] \right. \\
 & \left. + \left[\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot P_c \right. \right. \\
 & \left. \left. \frac{1_{K_{He}}}{18.01 \text{ g/mol}} \cdot \frac{(1.0 \text{ g/cc} \cdot V_w)}{18.01 \text{ g/mol}} \right] \right] \\
 / & \left[\frac{f_{K_{He}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}} + \frac{RT_f}{V_p} \right] \quad (74)
 \end{aligned}$$

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 moisture. 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:

$$I_w = S - \left(\frac{\frac{f_{K_{He}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}} \cdot S}{\frac{f_{K_{He}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}} + \frac{RT_f}{V_p}} \right) \quad (75)$$

Rearranging (75):

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

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:

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

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

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

$$\cdot \left[1 - \frac{\frac{f_{K_{He}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}}}{\frac{f_{K_{He}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}} + \frac{RT_f}{V_p}} \right] \quad (77)$$

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:

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

Under standard conditions this would equal:

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{P_{V_{\text{He}}}}{\text{STP } V_p} \quad (79)$$

where

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

$\text{STP } V_p$ = 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)).

$$I_p \cdot \frac{22414 \text{cc}}{1 \text{ mol}} = P_{V_{\text{He}}} \quad (80)$$

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, $\text{STP } V_p$, can be calculated by using Boyles and Charles laws:

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

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

$$V_p^{STP} = \frac{V_p P_f \cdot 273.16^\circ K}{T_f \cdot \text{latm}} \quad (82)$$

Substituting (82) into (79) yields:

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{P_{V_{He}}}{\frac{V_p P_f \cdot 273.16^\circ K}{T_f \cdot \text{latm}}} \quad (83)$$

Rearranging:

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{P_{V_{He}} \cdot T_f \cdot \text{latm}}{V_p P_f \cdot 273.16^\circ K} \quad (84)$$

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

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{I_p \cdot \frac{22414 \text{cc}}{1 \text{ mol}} \cdot T_f \cdot \text{latm}}{V_p \cdot P_f \cdot 273.16^\circ K} \quad (85)$$

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

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

$$\left\{ \frac{f_{K_{\text{He}}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}} \cdot \left[\frac{273.16^\circ \text{K}}{1 \text{ atm}} \cdot \frac{1 \text{ mole}}{22414 \text{ cc}} \right] \right.$$

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

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

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

$$\cdot \left(\frac{T_f \cdot 22414 \text{ cc} \cdot 1 \text{ atm}}{V_p \cdot P_f \cdot 1 \text{ mole} \cdot 273.16^\circ \text{K}} \right) \quad (86)$$

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

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

Rearranging equation (87):

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

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

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

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

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

Rearranging (88):

$$\begin{aligned}
 & \frac{\text{cc He}}{\text{cc pore space}} = \\
 & \frac{T_f}{V_p P_f} \left\{ \frac{22414 \text{ cc} \cdot \text{latm}}{1 \text{ mol } 273.16^\circ\text{K}} \left[\frac{273.16^\circ\text{K} \cdot 1 \text{ mol}}{\text{latm } 22414 \text{ cc}} \left[\frac{[Y] \text{cc He}}{10^6 \text{ cc air}} \cdot P_c \right] \cdot (V_h + V_p) \right. \right. \\
 & \left. \left. - \frac{5.240 \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \cdot P_f \right] + \left[\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot P_c \cdot \frac{(1.0 \text{ g/cc} \cdot V_w)}{18.01 \text{ g/mol}} \right] \right\} \\
 & \cdot \left[\frac{\frac{f_{K_{\text{He}}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}}}{\frac{f_{K_{\text{He}}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}} + \frac{RT_f}{V_p}}} \right] \quad (89)
 \end{aligned}$$

Multiplication and cancellation of equivalent terms yield:

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

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

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

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

and finally further cancellation and rearrangement yields:

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{T_f}{V_p P_f} \cdot \frac{1}{1 + \frac{RT_f V_w \cdot 1.0 \text{ g/cc}}{V_p K_{He} \cdot 18.01 \text{ g/mol}}} \left[\frac{[Y] \text{cc He}}{10^6 \text{cc air}} \cdot P_c \cdot (V_h + V_p) \right]$$

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

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

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.

$f_{K_{He}}^1$	=	Henry's Law constant, at temperature ($^{\circ}\text{C}$) 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 $^{\circ}\text{K}$)
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 ($^{\circ}\text{K}$)
$l_{K_{He}}^1$	=	Henry's law constant at temperature ($^{\circ}\text{C}$) 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 $^{\circ}\text{K}$

$$\frac{\text{cc He}}{\text{cc pore space}} = \frac{T_f}{V_p P_f} \cdot \frac{1}{1 + \frac{RT_f V_w}{V_p K_{\text{He}} \cdot 18.01}}$$

$$\left[\left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{T_1} \cdot (V_h + V_p) - \frac{5.24 \cdot 10^{-6} \cdot V_h \cdot P_f}{T_f} \right] \right. \\ \left. + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c \cdot V_w \cdot 22414}{K_{\text{He}} \cdot 18.01 \cdot 273.16} \right] \right] \quad (92)$$

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.

$$\frac{\text{cc He}}{\text{cc psp}} = \frac{T_f}{V_p P_f} X \left[\frac{1}{1 + \frac{RV_w T_f}{V_p f K_H X 18.01 \text{ g/mol}}} X \frac{\text{ppm He}}{10^6} \frac{P_c V_h}{T_1} \right]$$

$$+ \frac{\text{ppm He}}{10^6} \frac{P_c V_p}{T_1} - \frac{5.240 \text{ ccHe}}{10^6 \text{ cc air}} \frac{V_h P_f}{T_f} +$$

$$\left[\frac{\text{ppm He}}{10^6} \frac{P_c V_w X 22.414 \text{ l/mol} X 1000}{273.16^\circ\text{K} X 18.01 \text{ g/mol} X f K_H} \right]$$

Figure 9. Derived 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 $\times 10^6$ 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 $^{\circ}\text{C}$ in equation (92):

$$\begin{aligned} \text{ppm He} \times 10^{-6} &= \frac{\text{cc He}}{\text{cc pore space}} = \\ & \frac{(T_f + 273.16)}{V_p P_f} \cdot \frac{1}{1 + \frac{R (T_f + 273.16) \cdot V_w}{V_p f K_{\text{He}}}} \\ & \cdot \left[\left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c (V_h + V_p)}{(T_1 + 273.16)} - \frac{5.24 \cdot 10^{-6} \cdot V_h \cdot P_f}{(T_f + 273.16)} \right] \right. \\ & \left. + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c \cdot V_w \cdot 22414}{K_{\text{He}} \cdot 18.01 \cdot 273.16} \right] \right] \quad (93) \end{aligned}$$

where

cT_f = Temperature of soil at time of collection in $^{\circ}\text{C}$

cT_1 = Temperature of sample at time of analysis in $^{\circ}\text{C}$

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:

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

where

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

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°C) and an extreme soil temperature of 30°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:

$$\frac{P_{V_{He}}}{V_w} = \frac{\text{cc He}}{\text{cc H}_2\text{O}} \quad (95)$$

Substituting (94) into (95):

$$\frac{\text{cc He}}{\text{cc H}_2\text{O}} = \frac{I_w \cdot \frac{22414 \text{ cc}}{1 \text{ mol}}}{V_w} \quad (96)$$

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

yields:

$$\frac{\text{cc He}}{\text{cc H}_2\text{O}} = \left\{ \left[\frac{273.16^\circ\text{K} \cdot 1 \text{ mol}}{22414 \text{ cc}} \cdot \left[\frac{[Y] \text{ cc He}}{10^6 \text{ cc air}} \cdot P_c \right] \cdot (V_h + V_p) \right. \right. \\ \left. \left. - \frac{5.240 \text{ cc He}}{10^6 \text{ cc air}} \cdot V_h \cdot P_f \right] \right. \\ \left. + \left[\frac{[Y] \text{ cc He} \cdot P_c}{10^6 \text{ cc air}} \cdot \frac{(1.0 \text{ g/cc} \cdot V_w)}{18.01 \text{ g/mol}} \right] \right\} \\ \cdot \left[1 - \frac{\frac{f_{K_{\text{He}}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/cc}}}{\frac{f_{K_{\text{He}}} \cdot 18.01 \text{ g/mol}}{V_w \cdot 1.0 \text{ g/mol}} + \frac{RT_f}{V_p}} \right] \\ \cdot \frac{22414 \text{ cc}}{1 \text{ mole} \cdot V_w} \quad (97)$$

Simplifying (97) yields:

$$\frac{\text{cc He}}{\text{cc H}_2\text{O}} =$$

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

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

$$\cdot \left[1 - \frac{1}{1 + \frac{RT_f V_w \cdot 1.0 \text{ g/mol}}{V_p \cdot f_{\text{K}_{\text{He}}} \cdot 18.01 \text{ g/mol}}} \right] \cdot \frac{22414 \text{ cc}}{1 \text{ mol} \cdot V_w} \quad (98)$$

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 $\cdot 10^{-6}$):

$$\frac{\text{cc He}}{\text{cc H}_2\text{O}} = \left\{ \left[\frac{273.16}{22414} \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{T_1} \cdot (V_h + V_p) \right. \right. \right.$$

$$\left. \left. \left. - \frac{5.24 \cdot 10^{-6} \cdot V_h \cdot P_f}{T_f} \right] + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{l_{K_{\text{He}}}} \cdot \frac{V_w}{18.01} \right] \right] \right\} \cdot \frac{22414}{V_w} \quad (99)$$

$$\left[1 - \frac{1}{1 + \frac{RT_f V_w}{V_p l_{K_{\text{He}}} \cdot 18.01}} \right]$$

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 °C (instead of °K) the following correction must be made:

$$\begin{aligned}
 \frac{\text{cc He}}{\text{cc H}_2\text{O}} = & \left\{ \left[\frac{273.16}{22414} \cdot \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{(c_{T_1} + 273.16)} (V_h + V_p) \right. \right. \right. \\
 & \left. \left. \left. - \frac{5.24 \cdot 10^{-6} \cdot V_h P_f}{(c_{T_f} + 273.16)} \right] + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c \cdot V_w}{l_{K_{\text{He}}} \cdot 18.01} \right] \right\} \\
 & \cdot \left[1 - \frac{1}{1 + \frac{R \cdot (c_{T_f} + 273.16) \cdot V_w}{V_p \cdot f_{K_{\text{He}}} \cdot 18.01}} \right] \cdot \frac{22414}{V_w} \quad (100)
 \end{aligned}$$

where

c_{T_f} = Temperature of soil at time of collection in $^{\circ}\text{C}$

c_{T_1} = Temperature of sample at time of analysis in $^{\circ}\text{C}$

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 nonexistent (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:

$$\frac{\text{cc He}}{\text{cc H}_2\text{O}} = \left[\frac{273.16}{22414} \cdot \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{(c_{T_1} + 273.16)} \cdot V_h - \frac{5.24 \cdot 10^{-6} V_h P_f}{(c_{T_f} + 273.16)} \right] + \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c \cdot V_w}{l_{K_{\text{He}}} \cdot 18.01} \right] \right] \cdot \frac{22414}{V_w} \quad (101)$$

Simplifying (101):

$$\frac{\text{cc He}}{\text{cc H}_2\text{O}} = \frac{273.16}{V_w} \left[\frac{\text{ppm He} \cdot 10^{-6} \cdot P_c}{(c_{T_1} + 273.16)} \cdot V_h - \frac{5.24 \cdot 10^{-6} V_h P_f}{(c_{T_f} + 273.16)} \right] + \frac{\text{ppm He} \cdot 10^{-6} \cdot 22414 \cdot P_c}{l_{K_{\text{He}}} \cdot 18.01} \quad (102)$$

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 behavior, 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 ₂ O
Soil -- totally wet, no gaseous pore space	102	cc He/cc H ₂ O
Water	102	cc He/cc H ₂ O

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:

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

assuming 100% equilibration between added air and headspace volume
where

$$V_h = \begin{array}{l} \text{the amount of gaseous headspace in the sample container} \\ \text{(cc)} \end{array}$$

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:

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

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.	$\overline{6092} \pm 78$	$\overline{6464} \pm 55$	$\overline{8167} \pm 34$
11/12/82		6585	
	6196	6450	
	6166	6450	8410
	6106	6585	8352
	6076	6604	8448
Mean +/- Std. dev.	$\overline{6136} \pm 55$	$\overline{6535} \pm 78$	$\overline{8403} \pm 48$
11/22/82	6230	6856	
	6296	6839	8958
	6345	6790	8853
	6230	6856	8909
	6213	6873	8993
Mean +/- Std. dev.	$\overline{6263} \pm 56$	$\overline{6843} \pm 32$	$\overline{8928} \pm 61$
12/6/82	6215	6508	8090
	6079	6625	8090
	6099	6465	8206
	6099	6567	8206
	6099	6586	8206
Mean +/- Std. dev.	$\overline{6094} \pm 10$	$\overline{6550} \pm 64$	$\overline{8160} \pm 64$
12/16/82	5902	6272	
	5906	6452	8023
	5902	6511	8113
	5864	6228	8068
Mean +/- Std. dev.	$\overline{5894} \pm 20$	$\overline{6366} \pm 137$	$\overline{8068} \pm 45$
1/3/82	6112		7872
	6047		8013
	6112	6452	8013
	6099	6635	8060
	6047	6635	8060
Mean +/- Std. dev.	$\overline{6083} \pm 34$	$\overline{6574} \pm 106$	$\overline{8004} \pm 77$

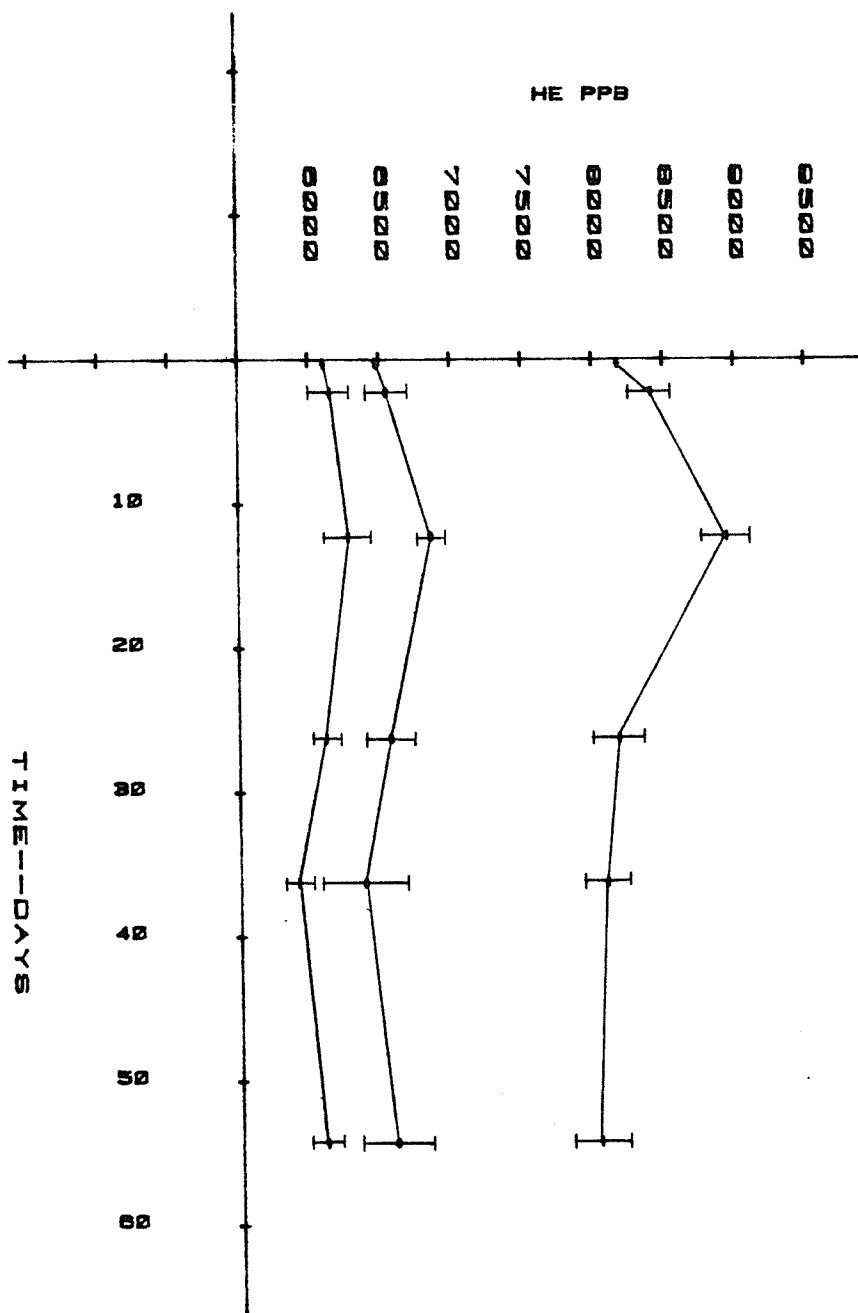


Figure 10. Graph of leakage test results over time.

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:

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

where

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

$V_{\text{res.}}$ = 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

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

and

$[\text{He}]_{\text{res.}}$ = 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:

$V_{\text{res.}}$ = 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

$[\text{He}]_{\text{meas.}}$ = 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 a 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 undoubtedly 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 occurred. 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 fluctuations 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 occurred 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 phenomenon 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

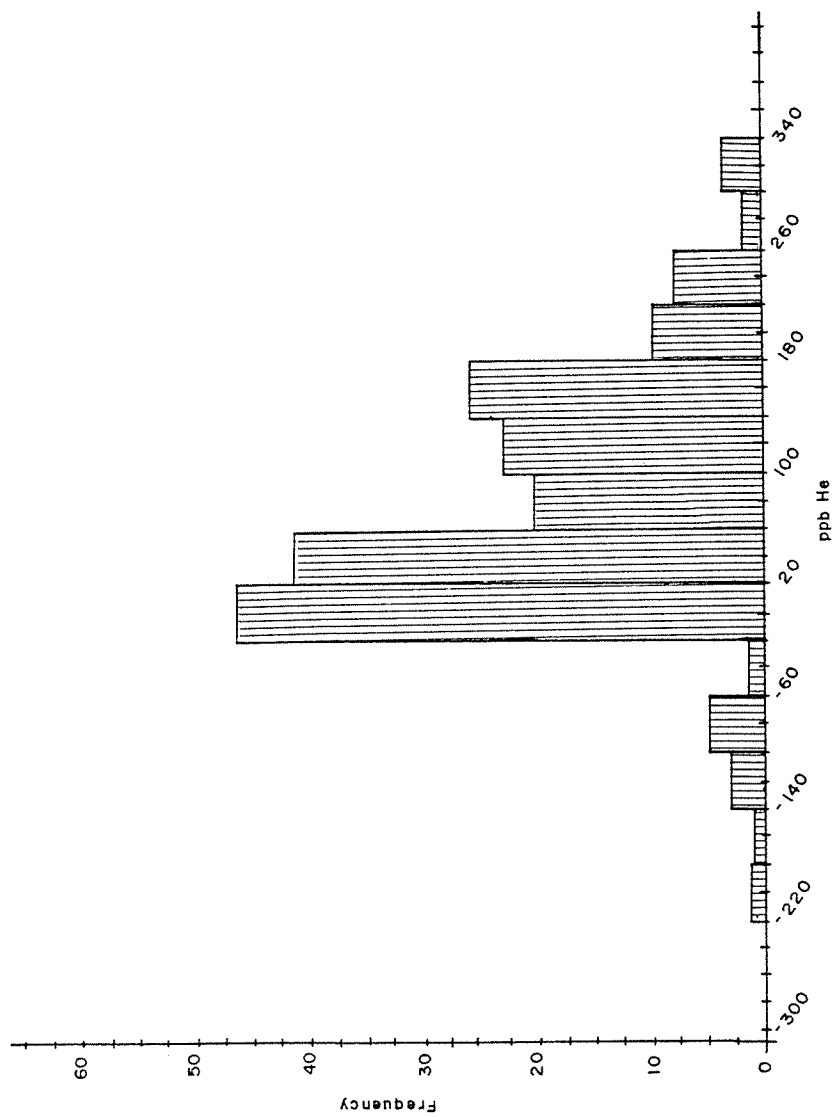


Figure 11. Frequency diagram of uncorrected helium in head-space concentrations for the Long Valley area.

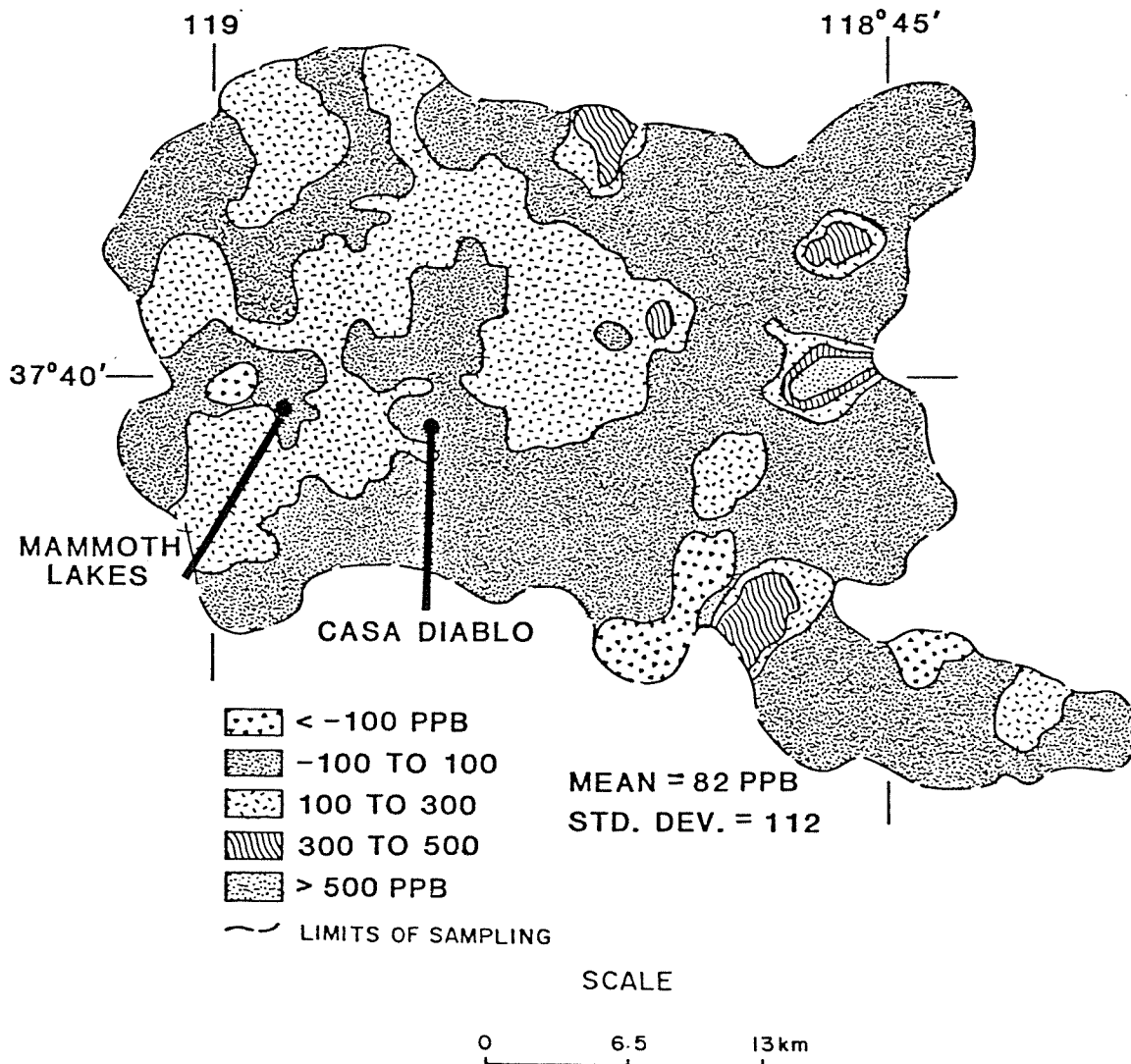


Figure 12. Smoothed contour map of uncorrected helium in headspace concentrations for the Long Valley area.

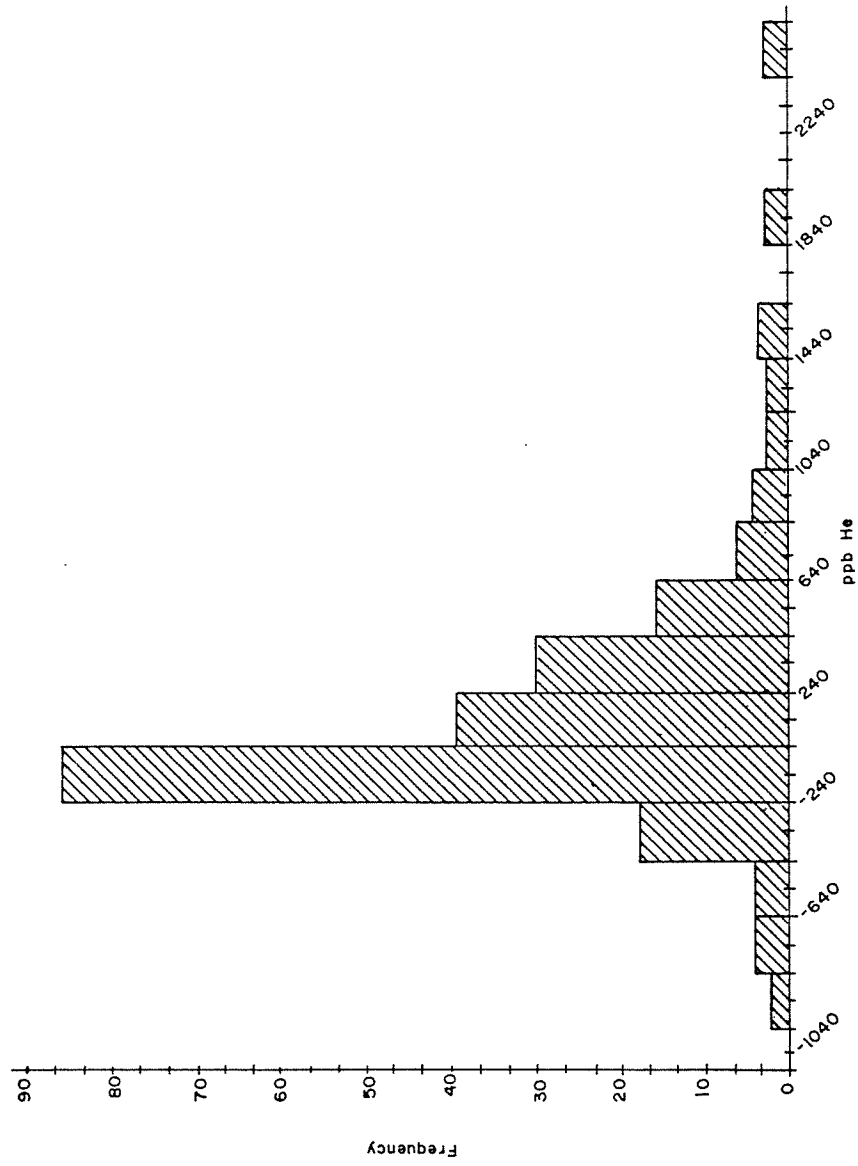


Figure 13. Frequency diagram of calculated helium in gaseous soil pore space concentrations, Long Valley.

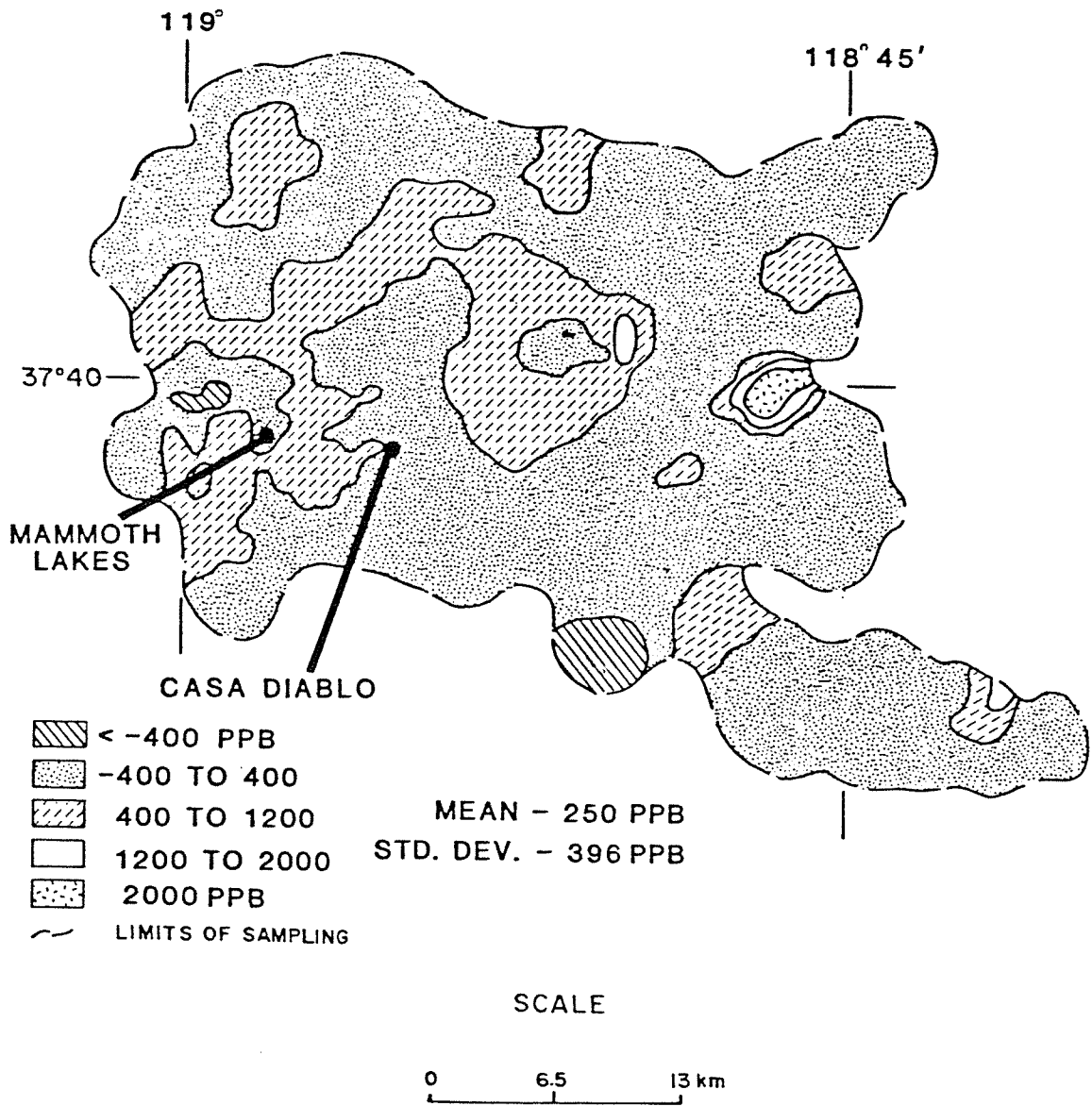


Figure 14. Smoothed contour map of helium in gaseous soil pore space concentrations for the Long Valley, area.

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_l
V_h	P_c	$l_{K_{He}}$
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°C = 5392.0	25°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 space.

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 thermodynamically 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°C	+/- 1.0°C	+/- 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°C	-1/0°C	+/- 0.0
P_c	0.80 atm	+/- .001 atm	+/- 12
K_{He}	1.4375x105	+/- 0.4 x 10 ⁵ mol H ₂ O/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° degree centigrade, introducing a possible error of $\pm 0.5^{\circ}\text{C}$ 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 $\pm 0.5^{\circ}\text{C}$. Summing these would give a possible total variation in the accuracy of the soil temperature measurement of $\pm 1.0^{\circ}\text{C}$. 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 $\pm 3.3 \times 10^{-3}$ 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