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**SOIL GAS EXPLORATION FOR MAGMA IN THE
CENTRAL RIO GRANDE RIFT, NEW MEXICO**

BY

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ABSTRACT

A soil gas survey was performed in an area of recent seismic activity near Bernardo, New Mexico. It has been suggested that the earthquakes in this area are due to the injection of magma into shallow levels of the crust. The objective of this study was to identify anomalously high concentrations of carbon dioxide (CO₂) and helium (He) degassed from magma emplaced at 4-7 km depth.

Samples collected with a soil gas probe were analyzed for CO₂ and He by gas chromatography, quadrupole mass spectrometry, and a He analyzer designed for leak detection.

Large variations in soil gas concentrations were observed throughout the study period. Values of CO₂ were as high as 26X atmospheric levels whereas He concentrations reached over 100 parts per billion (ppb) above normal atmospheric concentrations.

It is not certain that these anomalous soil gas readings are due to magma degassing. Permanent monitoring stations should be established in Bernardo and samples should be collected for carbon isotopic analyses and ³He/⁴He ratios to determine the true origin of these gases.

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INTRODUCTION

Recent studies of active volcanoes have shown they release significant amounts of carbon dioxide (CO₂) and helium (He) to the atmosphere [Sano et al., 1984; Chivas et al., 1987; Wakita et al., 1987; Williams et al., 1987; Fisher et al., 1990; Allard et al., 1991]. Gases are emitted primarily from main vent and crater fumaroles. This active degassing process was until recently assumed to be the dominant way by which volcanic gases were incorporated into the atmosphere.

Working at Vulcano Island, Italy, Baubron et al. [1990] have proved that flank emissions of gases through soils add substantial quantities of CO₂ and He annually to the atmosphere. By measuring soil gas concentrations of CO₂, Baubron et al. [1990] discovered that 30 tonnes/day of CO₂ was being released from the flanks of Fossa cone. This value, when compared to the 180 tonnes/day of CO₂ degassed from the central vent, is significant.

Volcanic gases are exsolved from magma bodies beneath areas of active volcanism due to a decrease in their solubility [Wakita et al., 1978; Sano et al., 1984; Tedesco et al., 1988; Torgersen, 1989; Baubron et al., 1990; Allard et al., 1991]. These gases then migrate through the crust to the earth's surface through fractures by the processes of mass transport and molecular diffusion [McCarthy and Reimer, 1986].

Pressure, temperature and melt composition all affect the amount of volatiles degassed. Pressure (depth) is the primary factor that controls the amount of gas which may be exsolved from a magma [Pan et al., 1991]. Upon ascent, a buoyant magma will exsolve gases as the result of decreasing lithostatic pressure. Depending upon the size and depth of the intrusive body, a sufficiently large quantity of volatiles may be degassed [Wakita et al., 1978].

Recent seismic investigations in the vicinity of Socorro, New Mexico indicate the existence of a sill-like body of magma at a depth of 19 km [Sanford et al., 1973]. This tabular, 1700 km² intrusion has been named the Socorro magma body (Fig. 1). Seismic swarms which have occurred in the area are thought to be caused by the emplacement of magma at shallow levels within the crust [Chapin, 1989].

Smaller diapirs derived from the Socorro magma body may be rising buoyantly through low-density sedimentary rocks. It is speculated that seismicity in the region is the result of the emplacement of these diapirs at depths of 4-7 km [Sanford, 1983].

I propose that the gases which are exsolved from these shallow magma bodies, such as CO₂ and He, may be detectable in the soils of the area. Using the technique of soil gas analysis, I have attempted to determine if gases of magmatic origin are diffusing through the soils to the atmosphere.

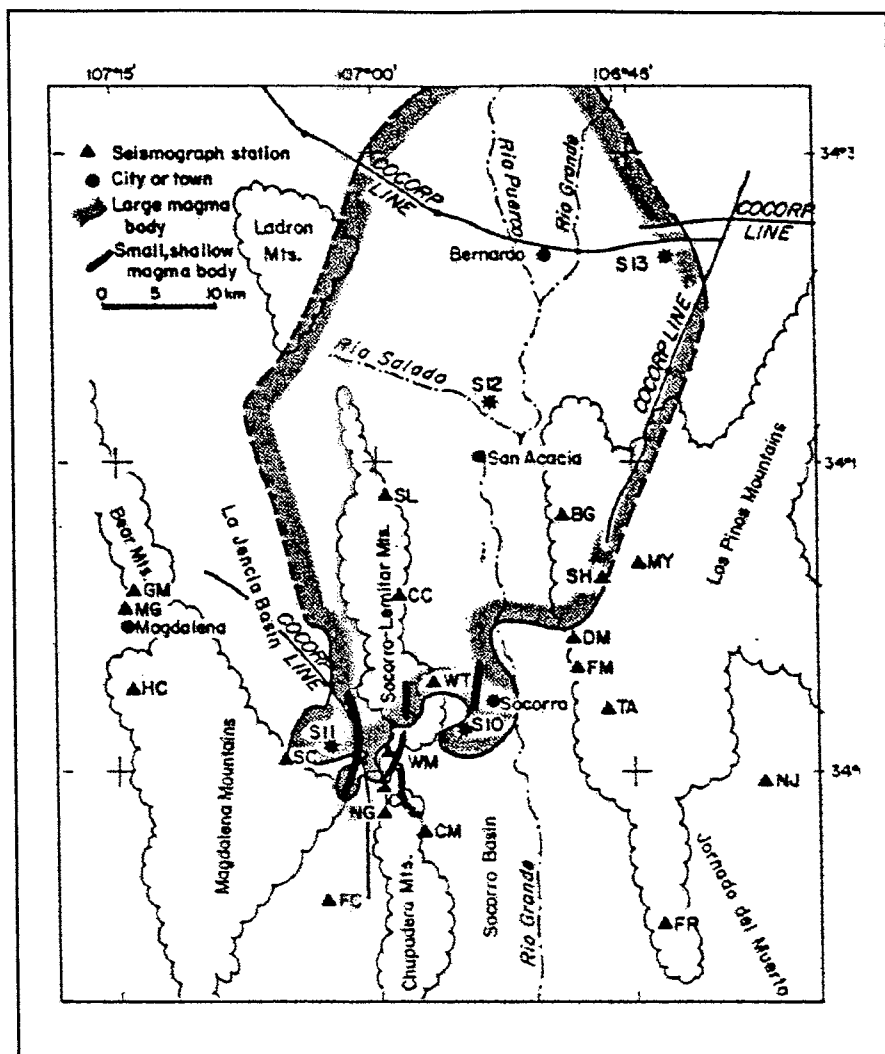


Figure 1: Areal extent of the Socorro Magma body (from Sanford, 1978).

The area chosen for study was located in Bernardo, New Mexico; a site of recent, frequent seismic activity (Fig. 2). Soil gases were collected in evacuated cylinders by means of a small-diameter hollow steel probe [McCarthy and Reimer, 1986]. Soil gas CO₂ profiles were obtained by making linear traverses across areas of intense seismic activity.

The samples were then returned to the New Mexico Institute of Mining and Technology campus for analysis by gas chromatography (GC) and quadrupole mass spectrometry (QMS). Additional samples were also analyzed at the USGS in Denver, Colorado using a He detector designed for leak detection.

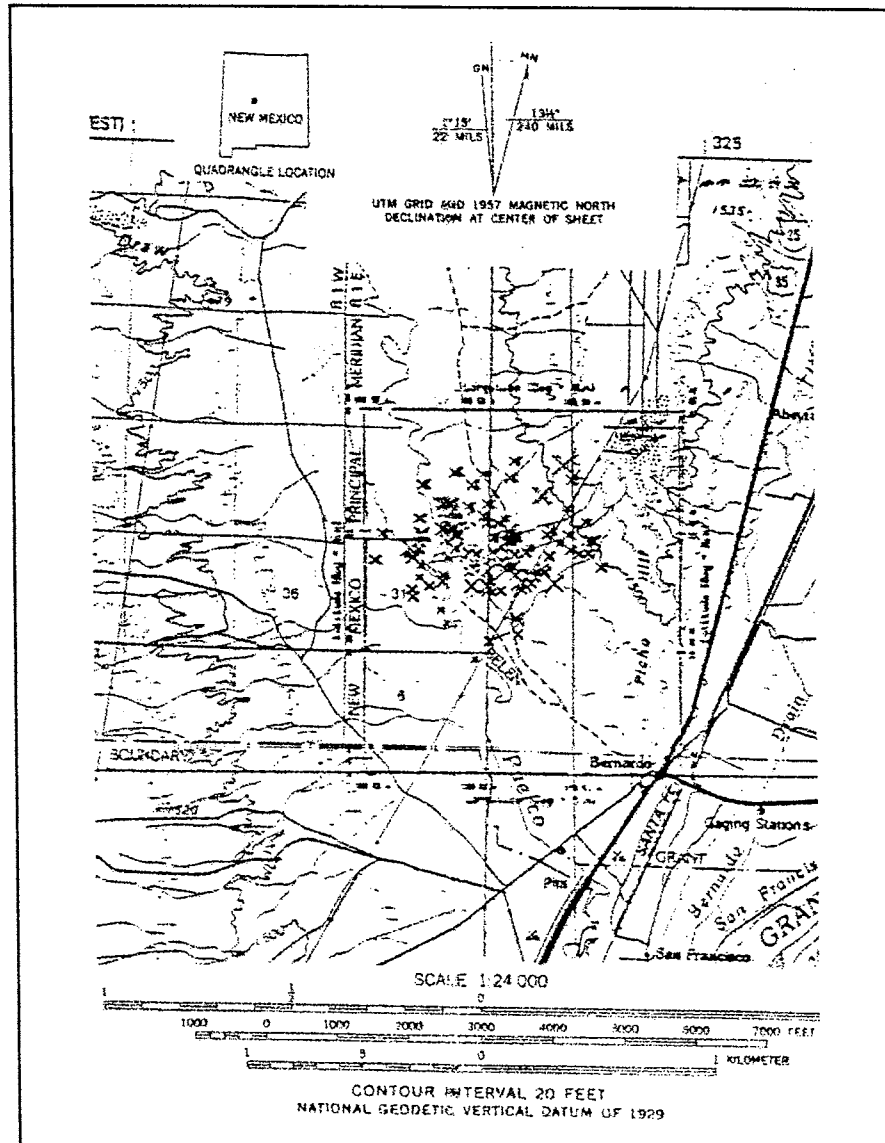


Figure 2: Seismicity in the Bernardo, New Mexico area. Largest X's represent earthquakes with the deepest focii (Sanford, pers. comm.).

SOIL GASES

Origins

Soil gases are contained in the pore spaces of soils, trapped on soil grain surfaces, or trapped or dissolved in soil water [Reimer, 1980]. Soil gases are either of primary or secondary origin [McCarthy and Reimer, 1986]. A soil gas is primary if its origin lies deep within the earth and is not produced in-situ. Secondary gases are produced within the soil realm and arise from the decay and respiration of biologic organisms [Anderson, 1982] and through inorganic processes such as the oxidation of sulfide bodies in carbonate-rich host rock [McCarthy and Reimer, 1986].

Current areas of volcanic activity such as mid-ocean ridges and oceanic island arcs are releasing significant amounts of gases to the atmosphere [Oxburgh and O'Nions, 1987; Wakita et al., 1987; Fisher and Perfit, 1990]. These gases include H₂O, CO₂, CO, O₂, CH₄, H₂S, H₂, He, Ar, HCl, SO₂, S₂ and HF.

Gases which were incorporated into the earth during its accretion are referred to as "primordial" [Ozuma and Podosek, 1983]. These gases, such as the rare gases, are valuable geochemical tracers due to their unique origin. Primordial gases have been used to infer the existence of magma chambers beneath active volcanoes and also as precursors of volcanic eruptions [Thomas et al., 1979].

Soil gases have been shown to be useful in geochemical prospecting [Brady and Rice, 1977; Alpers et al., 1990; Ball et al., 1990; Kesler et al., 1990; Reid and Rasmussen, 1990].

Gases such as CO₂, Rn and He are associated with distinct geologic environments and are valuable geochemical guides for locating specific mineral deposits.

Several gases appear in both volcanic and non-volcanic areas. A single gas alone is not sufficient to reach meaningful conclusions from soil gas data. The nature of some of the more important and most widely studied soil gases is discussed below.

Carbon Dioxide

Carbon dioxide is present at a concentration of 332 parts per million (ppm) in the atmosphere [Bremner and Blackmer, 1982]. It is also present in soil gases and may be either a primary or a secondary gas.

Recent research on tholeiitic basalt magmas has shown these bodies contain large amounts of dissolved CO₂ [Pan et al., 1991]. Solubility studies indicate that CO₂ is insoluble in basaltic magma and exsolves even under 5-10 kilobars pressure [Bottinga and Javoy, 1991]. For this reason, CO₂ is anticipated to be a major constituent of soil gas in areas of active volcanism.

Baubron et al. [1990], working at Vulcano Island, Italy recently found that CO₂ is diffusing through the flanks of Fossa cone at a rate of approximately 30 tonnes per day. He/CO₂ and ¹³C/¹²C ratios have shown similar origins between fumarolic gases and flank soil gases. Until the time of this study most researchers did not take into account the contribution of non-fumarole CO₂ to estimates of earth's CO₂ budget.

It is now widely accepted that non-eruptive emissions contribute more CO₂ to the atmosphere annually than do explosive eruptions [Gerlach, 1991].

Gerlach [1991] has compiled data on the CO₂ emission rates for select subaerial volcanoes (Table I, Appendix I). Mount Etna emits the greatest amount of CO₂ of any volcano listed. By comparison, CO₂ emissions from Vulcano Island measured by Baubron are several orders of magnitude smaller. When considering the earth's CO₂ budget, the significance of CO₂ added to the atmosphere by quiet degassing cannot be ignored.

In non-volcanic regions, CO₂ is produced mainly through the oxidation of sulfide bodies by acidic groundwaters in carbonate environments [Reid and Rasmussen, 1990]. During this process, CO₂ is produced and O₂ is consumed.

Helium

The noble gas helium is the second most abundant element in the solar system. Its present concentration in the earth's atmosphere is 5240 parts per billion (ppb) [Glueckauf, 1946]. Due to its inertness, low atmospheric concentration and ease of diffusion, He is widely employed in the study of active volcanic processes [Wakita et al., 1978; Williams et al., 1987; Torgersen, 1989; Hinkle, 1991] and earthquake prediction [Reimer, 1985].

There are two isotopes of helium and they differ significantly in their origins and relative abundances [Ozima and Podosek, 1983]. ³He is a primordial gas which is derived mostly

from the earth's interior (minor amounts of ^3He are present in the atmosphere due to the decay of tritium generated by nuclear weapons testing) [Oxburgh and O'Nions, 1987]. By comparison, ^4He is a decay product of ^{238}U , ^{235}U , ^{232}Th and ^{40}K . The ratio $^3\text{He}/^4\text{He}$ for the earth's atmosphere is expressed as R_a , which has a present day value of 1.40×10^{-6} [Williams et al., 1987; Wakita et al., 1987]. Values of R_a which are considerably larger than 1.40×10^{-6} have been used to indicate the presence of mantle derived helium in areas of continental volcanism and at mid-ocean ridges [Allard, et al., 1991; Fisher and Perfit, 1990; Sano and Wakita, 1988].

Lombardi and Reimer [1990], working in the Phlegraean Fields of Italy, delineated pathways of migration for volcanic gases. Their study consisted of 270 soil gas samples over an area of 45 km^2 . Samples were analyzed for ^4He and ^{222}Rn . The survey area was chosen to coincide with many major structural features of the region such as collapsed caldera rims and faults. Lombardi and Reimer [1990] were able to discern fault traces and the boundaries of collapsed caldera rims by plotting soil gas He and Rn values on maps and contouring the data. No correlation was found between He and Rn concentrations. Significantly high He values at a sample site often displayed very low Rn values for the same sample. Another interesting result of this study was that near surface rocks of different chemical compositions did not influence the data.

High concentrations of He in soil gases cannot be attributed unquestionably to volcanic processes. Granitic rocks contain large quantities of radioactive U and Th and often emanate haloes of He and mercury (Hg) which can be detected in soils [Fursov, 1990].

Migration of Gases Through Soils

Gases migrate through soils by the process of molecular diffusion and mass transport [McCarthy and Reimer, 1986]. Many factors affect the diffusion of gas molecules through soil. Barometric pressure, soil moisture and wind all influence soil gas concentrations to some degree [Reimer, 1980; Hinkle, 1991].

Fick's Law describes the behavior of migrating gas molecules through soils [de Jong and Schappert, 1972; Wood and Petraitis, 1984; Solomon and Cerling, 1987]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(D_s \frac{\partial C}{\partial z} \right) + \alpha$$

where C is the concentration of the gas, t is time, D_s is the diffusion coefficient of the gas in the soil, z is soil depth and α is the production or consumption rate of the soil gas.

The diffusion coefficient of the soil gas at a specified temperature relative to its diffusion rate in air is given by:

$$D_s = D \theta \mu$$

where D is the diffusion coefficient in air, θ is the air-filled soil porosity and μ is the empirically derived tortuosity factor. Steady-state soil gas diffusion is defined by:

$$-q - Ds \frac{\partial C}{\partial z} + \alpha$$

where q is the gas flux.

Factors Affecting Soil Gas Concentrations

The physical characteristics of a soil as well as environmental factors all affect soil gas concentrations [Bremner and Blackmer, 1982; Reimer, 1986; Hinkle, 1991]. External factors in the environment which may increase or decrease soil gas concentrations include barometric pressure, air temperature, wind speed, soil temperature and moisture, relative humidity, and precipitation.

Reimer [1980] collected soil gases from 3 sites in North America and analyzed for He. Samples were collected during times of varying environmental conditions and at different soil depths. A strong correlation was found between increased soil gas He and high soil moisture. He speculated that the soil moisture acted as a "cap" trapping He and slowing its escape to the atmosphere.

A relationship between high wind speeds and decreased soil gas He was observed. Wind blowing over the soil surface created a Bernoulli effect which pumped gases from the soil, thereby lowering its concentration. It was discovered that temperature gradients at the soil-atmosphere interface also can create a local "pumping effect". These pumping effects are also very dependent on the soil porosity and soil type.

Reimer [1980] found that He values were only slightly influenced by wind speed and soil moisture below 1 m depth. Environmental variables observed to have little or no effect on soil gas values were barometric pressure, soil temperature, and relative humidity.

Secondary gases can be produced through organic processes [Bremner and Blackmer, 1982; Amundson and Davidson, 1990]. Different forms of vegetation contribute to soil gas anomalies. Carbon dioxide is produced in soils by decaying organic matter. Aerobic respiration by plant roots and microorganisms produces CO_2 and consumes O_2 [Amundson and Davidson, 1990]. These types of variations in soil gases are influenced greatly by diurnal and seasonal fluctuations.

GEOLOGY

Central Rio Grande Rift

The Rio Grande rift is a narrow, linear feature comprised of asymmetrical basins formed as the result of extensional forces (Fig. 3). From its northern boundary in central Colorado to its terminus in Chihuahua, Mexico, the rift measures more than 1000 km in length [Olsen, et al., 1987]. Although closely related in time and space to the Basin and Range province, the rift is a unique geological feature.

En-echelon, fault-bounded basins comprise the overall structure of the rift [de Voogd et al., 1986; Hermance and Neumann, 1991]. Basins take on the form of half-grabens whose steeply dipping fault surfaces form the faces of the regions many mountain ranges.

Geophysical surveys have determined that the asthenosphere is presently in contact with the base of the crust beneath the rift [Olsen et al., 1987]. The Moho lies at a depth of 45 km at the edge of the rift whereas along its axis the depth is 33 km. Seismic velocities (P_n -waves) range from 7.6-7.8 km/s, indicating anomalously high temperatures at depth.

Near Socorro, a major transfer fault or accommodation zone trends nearly perpendicular to the main rift axis [Chapin, 1989]. The Socorro accommodation zone (SAZ) separates fault blocks which dip in nearly opposite directions. This structure's development is thought to have been controlled by the existence of the prerift Morenci lineament.

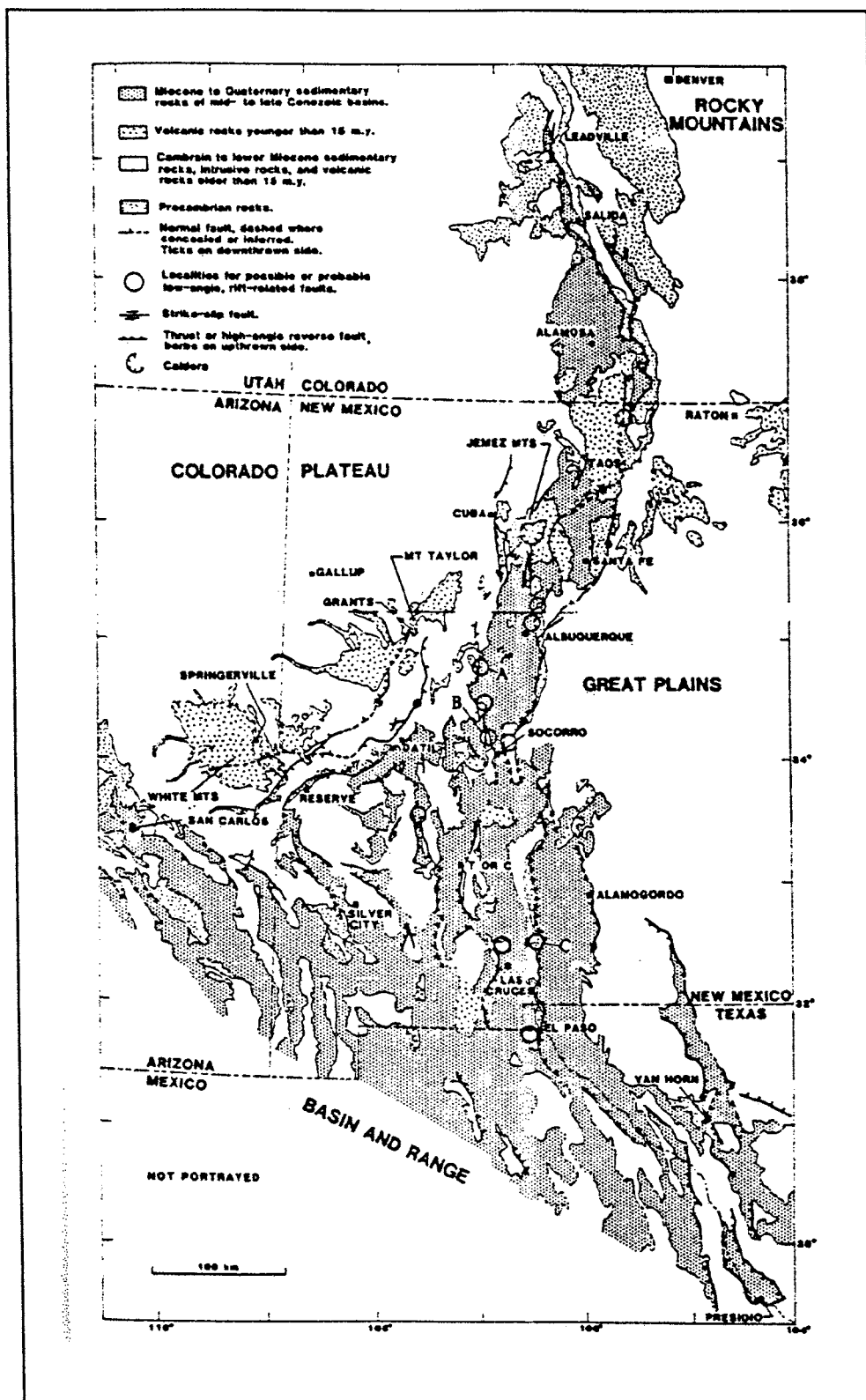


Figure 3: Overview of Rio Grande rift (from Olsen et al., 1987).

Eruptions of large quantities of magma occurred during the first stages of rifting in the Socorro region [Chapin, 1989]. Rhyolitic magmas were extruded more commonly than were mafic. The Hells Mesa tuff, erupted around 32 Ma, is essentially the boundary line between prerift and synrift volcanism. Rapid extension was initiated in this part of the rift at approximately 29 Ma. Immense volumes of silicic ash-flow tuffs and mafic lava flows occur from 28.9-27.3 Ma. Bimodal volcanism near Socorro is common from 24.3 to 3.6 Ma.

The Rio Grande rift does not fit easily into either a passive or active continental rift framework. Compared to other continental rifts it is relatively "dry", lacking voluminous volcanic deposits. Compositions of basalts within the rift range from alkalic to tholeiitic. No trend in compositions exists either spatially or temporally [Olsen et al., 1987].

Socorro Magma Body

During 1973, seismic investigations first revealed a major crustal reflector near the Conrad Discontinuity at a depth of 19.2 ± 0.6 km within the central Rio Grande rift near Socorro [Sanford, 1973; Brocher, 1981]. The initial evidence for the mid-crustal magma body was the reflection of microearthquake S-waves from the top of the structure. Later studies in 1976 by the Consortium for Continental Reflection Profiling (COCORP) also identified a strong mid-crustal reflector at 19 km depth [de Voogd et al., 1986].

The region surrounding Socorro is the most seismically active part of the Rio Grande rift [Olsen et al., 1987]. Earthquakes of magnitude -0.5 to 4.0 have occurred in this century [Sanford et al., 1983]. Many of the earthquakes occur in swarms and show compressional first motions similar to those which are associated with present volcanic activity in areas such as the Japanese islands [Wakita et al., 1987].

The small diapirs emplaced at 4-7 km which are inferred to be responsible for the seismicity near Socorro are most likely originating from the mid-crustal magma body. If this hypothesis is true, after differentiating or by migrating along fractures, these bodies rise buoyantly to shallow levels within the crust. Seismicity in the region could be reconciled with the injection of magma along normal faults on the order of 50 m in width [Chapin, 1989].

Associated with the intense seismic activity of the area is a pronounced crustal doming [Reilinger and Oliver, 1976; Larsen and Reilinger, 1986] (Fig. 4). Maximum crustal uplift is situated 25 km north of Socorro [Larsen et al., 1983]. Railroad survey profiles indicate the uplift has been occurring since at least 1918 and perhaps as early as 1880 [Ouchi, 1983]. Uplift rates derived from these cross-sections are on the order of 5-18 mm/yr.

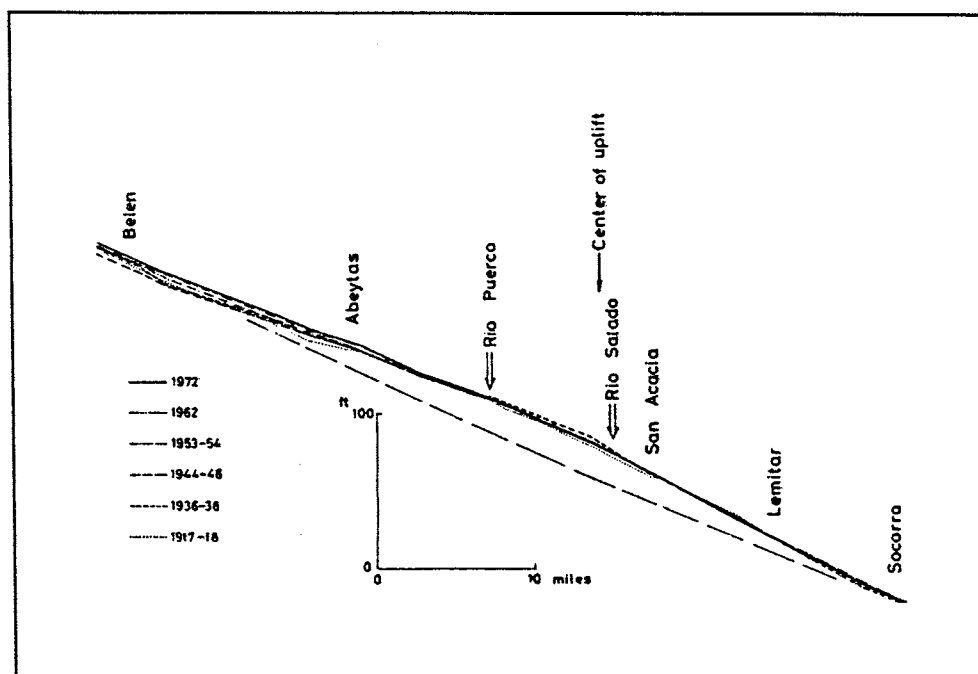


Figure 4: Uplift over the Socorro magma body due to the injection of magma at depth (from Ouchi, 1983).

Ouchi [1983], investigating the Loma Parada terrace gravels, arrived at a rate of uplift of 1.8 mm/yr. This figure is based on a 37 m incision of the terrace caused by the Rio Grande in gravels which are 20,000 years old.

To explain this rate of crustal swelling, magma would have to be emplaced at a rate of 10^{-2} km³/yr [Sanford and Einarsson, 1982].

Current estimates place the magma body's areal extent at a minimum of 1700 km² and its thickness at approximately 150 m [Ake and Sanford, 1988]. A two layer model for the vertical structure of the magma body is most consistent with the P-wave arrival data. The uppermost layer is on the order of 70 m thick

while the underlying, denser layer is 60 m thick. This lower, more dense layer may be an accumulation of crystals settling under gravity's influence, or the remnants of a previously solidified magma body.

Seismic data reveals that the surface topography of the magma body is relatively planar. However, uncertainty in seismic reflection data allows relief of up to 0.8 km. A small component of northward dip is likely but does not exceed more than 2° [Sanford, 1988]. Arrival times of P-waves give evidence of extreme lateral changes in internal structure [Brocher, 1981].

The composition of the magma body is unknown but is assumed to be basaltic. This is based primarily on the physical dimensions of the body [Chapin, 1989]. Most voluminous lava flows in this part of the Rio Grande rift are basaltic in composition. Arguing by analogy, it is widely believed the composition of the Socorro magma body is similarly mafic.

Chapin [1989] believes the composition of the smaller, shallow diapirs at 4-7 km to be felsic. His argument is that before these smaller magma bodies can rise buoyantly, they must become less dense than their parental body. Trapping of magma between layers of different density could allow a mafic magma to produce felsic melts [Glazner and Ussler, 1988]. This could be accomplished through fractional crystallization of regions of the main magma body. After differentiation and corresponding decrease in density, the newly formed felsic melt may rise through the crust.

The age of the magma body is uncertain. Theoretical studies based on the physical characteristics of the magma body place its age between 75,000 and 105,000 years. If the magma chamber is somehow being supplied with fresh magma from the mantle its age may be substantially older [Huppert et al., 1986].

Model of Basaltic Magma Degassing

The factors affecting magma degassing are primarily confining pressure and melt composition. If values for these parameters could be found it would be possible to develop a computer program to calculate the amount of CO₂ exsolved from the Socorro magma body. A reasonable estimate of the lithostatic pressure exerted on the body at 19 km depth can be derived from the simple $P=\rho gh$ relationship. Melt composition can be assumed to be similar to modern day tholeiitic basalts. Given sufficient knowledge of initial conditions, it is possible to quantitatively determine the amount of gas exsolved from a buoyantly ascending diapir.

Following the above criteria, a computer program was developed to simulate the exsolution of CO₂ from a basaltic magma. The purpose of the program was to gain an understanding of the size of the soil gas anomaly which may exist in the study area. The PASCAL program *Solubility* and its output appear in Appendix I.

The initial CO₂ content of the magma was estimated by using an average modern day tholeiitic basalt composition [Pan et al., 1991]. It was assumed the magma body was saturated with CO₂.

The solubility of CO_2 , which was entirely pressure dependent, was calculated using an equation developed by Holloway [1991].

The model begins by entering the greatest depth for the magma. The pressure is decreased on the magma body by decreasing its depth at any desired increment. The resulting wt% of CO_2 exsolved is then calculated by subtracting the CO_2 solubility at the final depth from its solubility at the initial depth.

An absolute gas amount was derived by assuming a magma density of 2.6 gm/cm^3 . The quantity of CO_2 exsolved from a magma as it ascends from 19 km to 6 km was obtained from the Solubility program. The amount of CO_2 degassed during this 13 km interval was 0.394 wt%. Multiplying the wt% CO_2 exsolved by the density of the magma gave a value of $1.02 \times 10^4 \text{ gm CO}_2/\text{m}^3 \text{ magma}$ ($2.33 \times 10^2 \text{ moles CO}_2/\text{m}^3 \text{ magma}$).

The model shows that a significant amount of CO_2 is exsolved even at depths on the order of 6 km (Fig. 5). Any upward movement of the body decreases its overburden pressure and causes a decrease in CO_2 solubility.

This model may underestimate CO_2 exsolution by assuming tholeiitic composition. Many of the basalts in the Rio Grande rift are calc-alkaline in composition [Kelley and

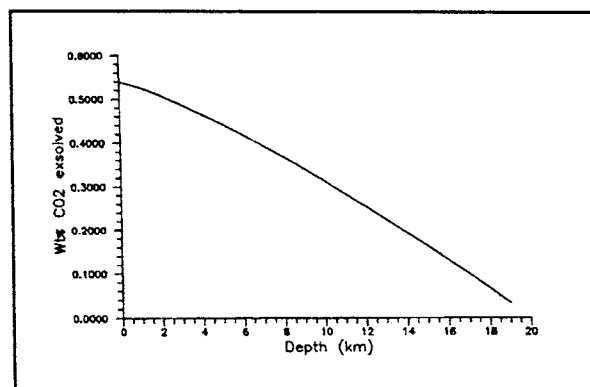


Figure 5: Graph of CO_2 solubility vs. depth for a basaltic magma.

Kudo, 1978]. Alkalic magmas contain substantially larger amounts of dissolved CO₂ [Bottinga and Javoy, 1991]. Therefore, the model is at best a minimum estimate of the amount of CO₂ which may be degassed.

STUDY AREA

Bernardo

Bernardo lies 25 mi (km) north of Socorro along New Mexico Interstate 25. The study site is bounded by the Sevilleta Wildlife Refuge to the south and I-25 to the east. Elevations at the area of investigation range from 1400-1500 m above mean sea-level.

Young alluvial materials from the Rio Puerco form terrace deposits in this area such as Llano de Albuquerque (Fig. 6) [Machette, 1983]. The Pliocene Sierra Ladrones formation is the only Tertiary unit to outcrop at the study area.

The area of investigation is relatively flat and occupies the site of an ancient playa lake. Several north-south trending normal faults are present to the west and southwest of the study area.

Soils

The soils of the Bernardo area are a sandy loam with minor amounts of clay. After a period of rain the soil becomes polygonally cracked due to the presence of expandable clays.

Vegetation

Creosote, sagebrush and various cacti are the forms of vegetation found in abundance in the study area. Farther west small junipers can be found inhabiting the banks of arroyos. Portions of the site have been and are still extensively grazed by livestock.

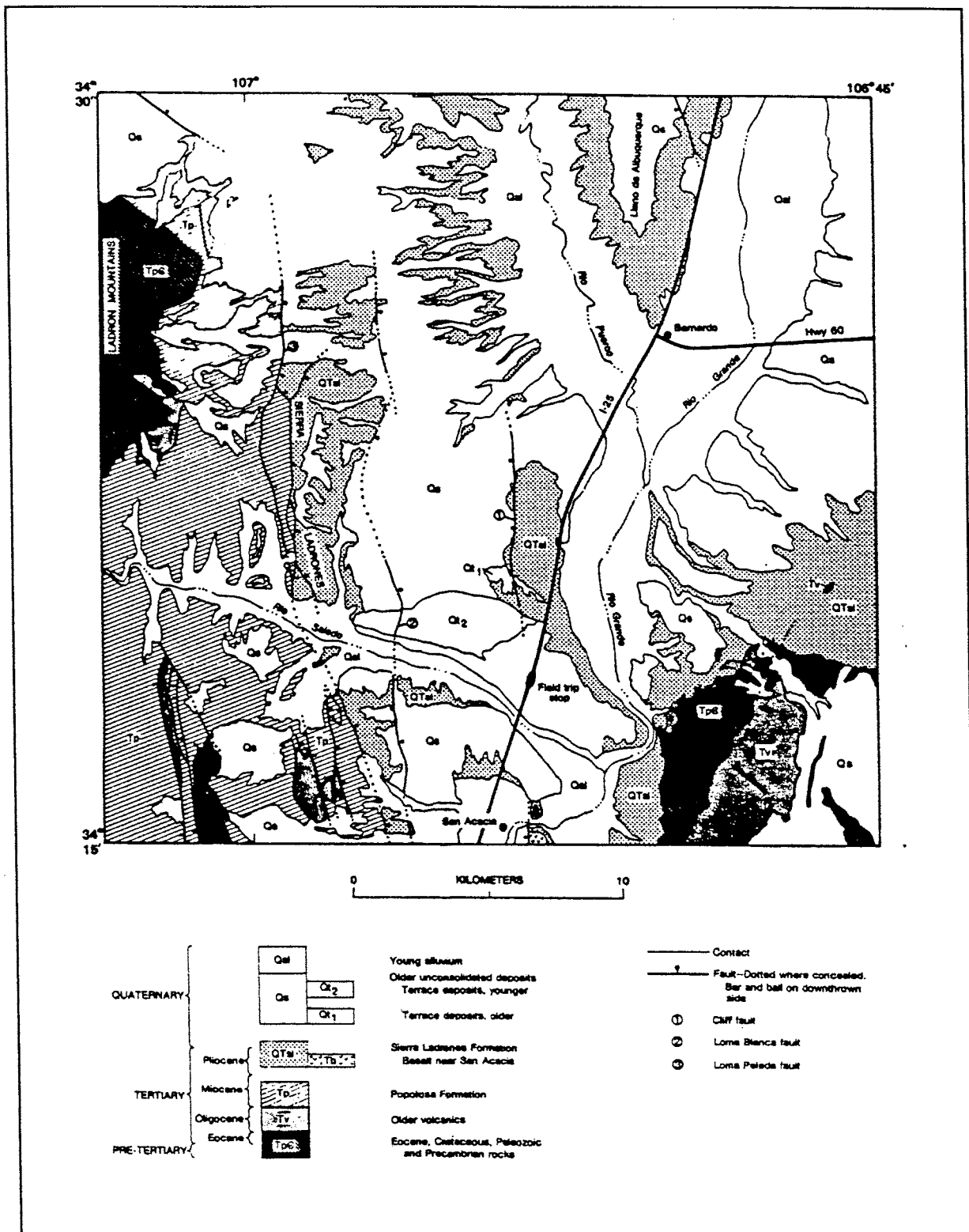


Figure 6: Geologic map of the Bernardo, New Mexico area (from Machette, 1982).

METHODS OF INVESTIGATION

Sample Locations

Sample intervals of 0.25 mi., (0.42 km), shown as triangles, and 0.10 mi., (0.17 km), shown as black dots, were used in collecting soil gas samples. The sampling interval was measured by recording distances on an automobile odometer. Samples were collected near the edge of a dirt road which lead westward from the Bernardo interchange along I-25 at exit 175 (Fig. 7). The sample line was located directly over the epicenters of the most recent and strongest earthquakes in the region.

To insure soil gas anomalies were real and not simply measurements of normal background, two baselines were established; one south of the main line (Fig. 7) and the other near San Antonio, New Mexico (Fig. 8).

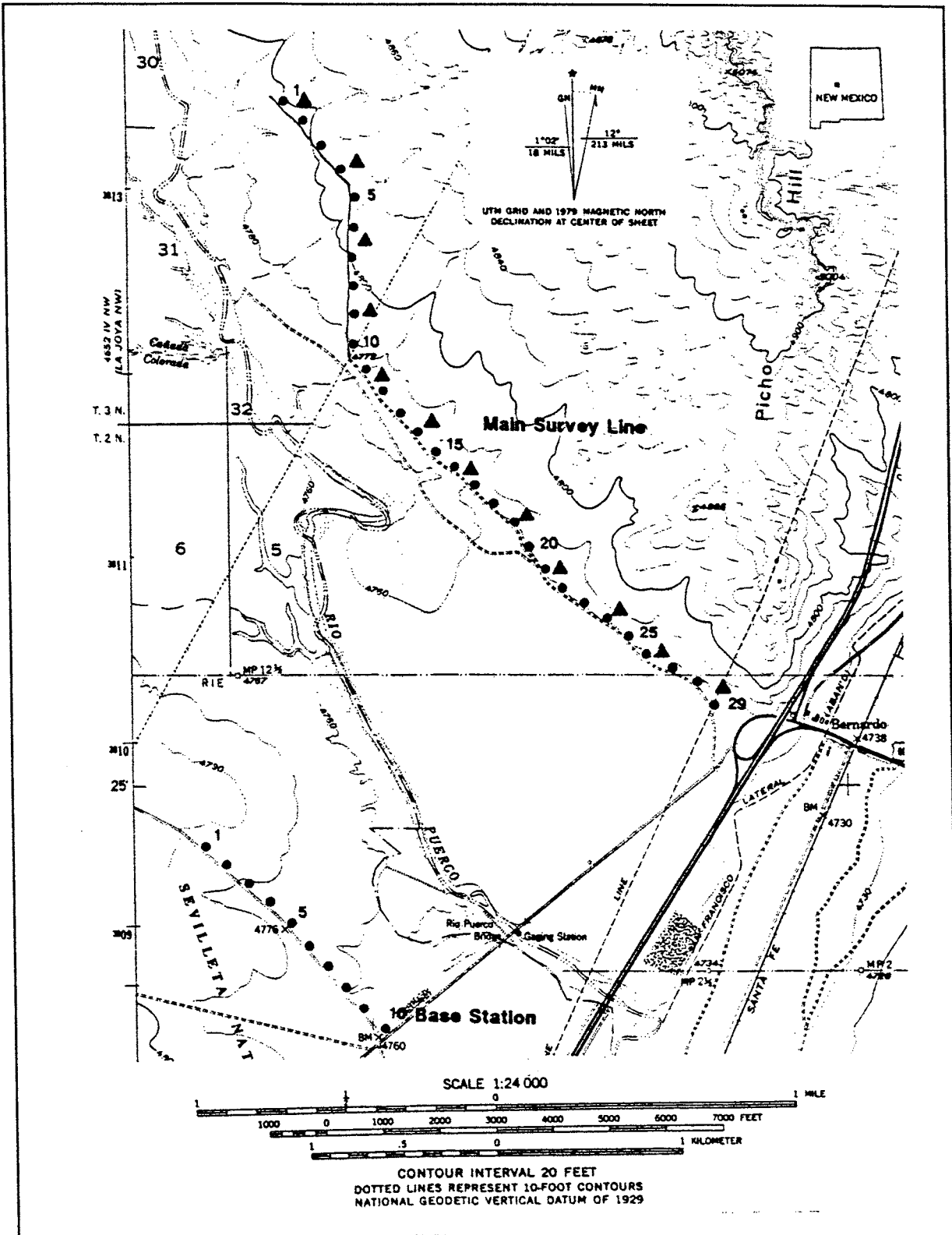


Figure 7: Site map showing sample locations and base line.

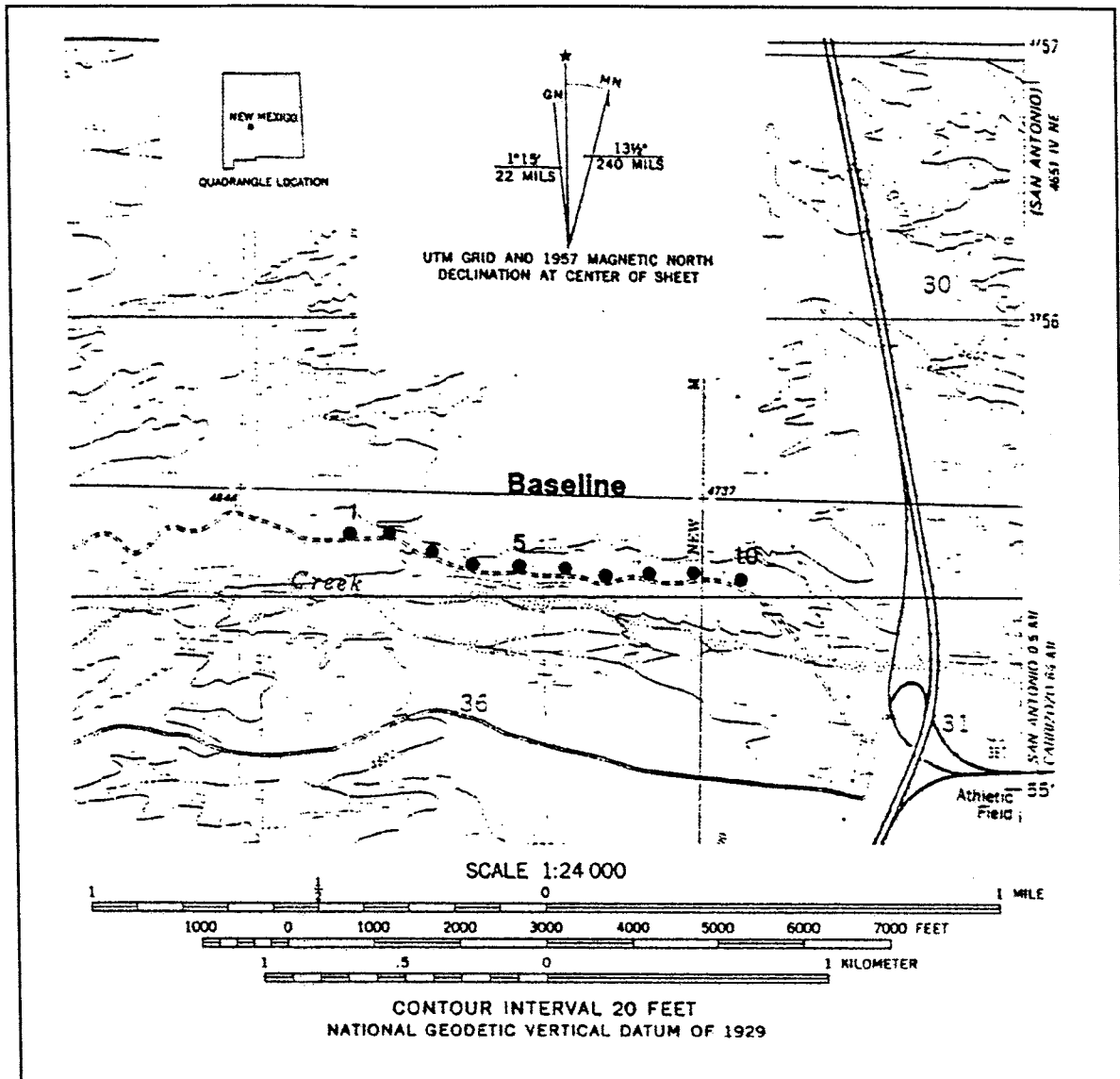


Figure 8: Base line at San Antonio, New Mexico showing sample locations.

Sampling Procedure

Soil gas samples were collected by driving a hollow steel probe into the ground to a depth of 0.75 m [McCarthy and Reimer, 1986]. The probe was a rigid 1 m length steel tube with an inside diameter of 1.59 mm (Fig 9). A split-hammer mounted cylindrically around the outside of the probe was used to pound the probe to

the desired depth. The impact of the hammer upon the lower stop of the probe provided sufficient force for penetration of the soil. This probe had 10 holes drilled into its side near the base to allow entry of soil gas. A 1.50 mm outside diameter wire was inserted into the probe during its emplacement in order to keep soil from clogging the gas inlet holes.

A septum-holder was attached to the top of the apparatus. This fitting contained an o-ring which made an air-tight fit around the top of the probe. The probe was then purged of atmospheric contamination by inserting a needle through the septum on top of the probe and removing 10 cc of gas with a syringe.

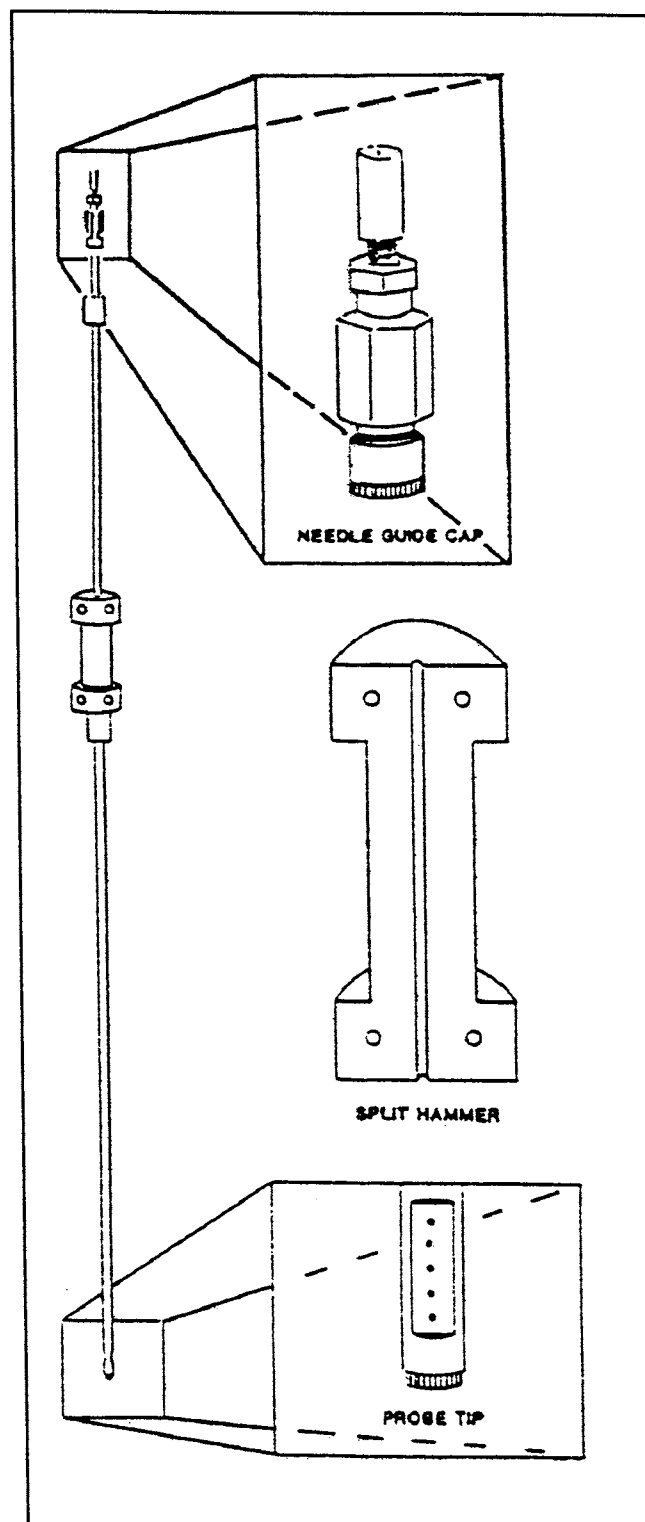


Figure 9: Schematic of soil gas probe (from Reimer, 1990).

The soil gas sample was then collected in the same manner and transferred to pre-evacuated cylinders.

Vacutainer brand evacuated vials were used for sample collection as were stainless-steel cylinders. The vacutainers and steel cylinders had a volume of 10 cc and 5 cc respectively. Vacutainers are commercially available glass blood-collection vials with red rubber septa. The cylinders were made of stainless steel.

Samples were injected into the pre-evacuated steel cylinders by inserting a syringe through a septum which was isolated from the rest of the container by a valve. The vacuum present in the cylinder was allowed to draw down the syringe plunger to around the 5 cc calibration mark. The remaining sample was forced into the cylinder which slightly over-pressured the unit.

Analytical Procedure

Gas Chromatography

Laboratory analyses were performed on a Varian 3600 gas chromatograph (GC) which was equipped with a Poropak 'Q' column heated to 40° C. The filament temperature was set at 160° C while the injector and detectors were both adjusted to 110° C. Helium was used as the carrier gas. The helium and sample were both flowing through the column at 300 psi.

A 1 cc soil gas sample was injected through a silicon septum into the GC using a Hamilton gastight syringe. The GC identified gases by means of their retention times. The retention time for CO₂ was on the order of 3 to 5 minutes.

Peaks were recorded on a Hewlett-Packard #3396-A integrator. This automatically calculated the peak areas and percent of total peak area for each gas species present in the sample and provided a printout of the data (Fig. 10). Peaks most prominently recorded were air, CO₂ and a minor amount of CH₄. The peak areas were later normalized to atmospheric concentrations.

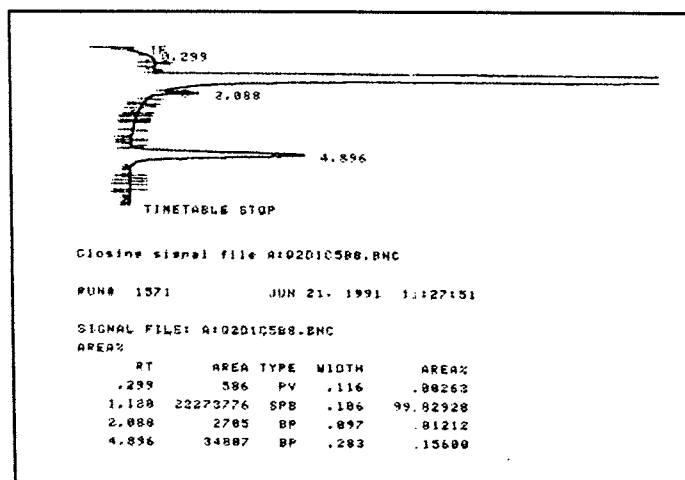


Figure 10: Peaks recorded by GC integrator. Off-scale peak is air with minor CH₄ spike. Peak at 4.896 mins. is CO₂.

A calibration curve was constructed in order to quantitatively determine the amount of CO₂ present in each sample. This was done by injecting a known volume of pure CO₂, taken from a laboratory gas cylinder with a syringe, into the GC. This procedure was repeated a sufficient number of times until a graph of response vs. volume was generated. From this graph it was later possible to determine the CO₂ concentration in the soil gas sample.

Quadrupole Mass Spectrometry

The quadrupole mass spectrometer operates on the principle of separation of different gases based on their relative masses. Separation is accomplished by passing the gases through the quadrupole's orthogonal magnetic fields which vary in intensity. The quadrupole is sensitive to ± 1 ppm.

Samples were injected through a teflon septum into an isolated section of a glass vacuum line. After being allowed to equilibrate, the gas was expanded through the remainder of the vacuum line. A cold finger made of a solid CO₂ (dry ice) and ethylene glycol mixture was used to trap any water vapor which may have been present in the sample.

Once gas entered the mass spectrometer, a personal computer with the program Quadstar recorded intensities of various gases. Up to 10 channels were scanned simultaneously and displayed as histograms.

The height of each histogram was proportional to the concentration of the mass number being scanned. The computer also recorded relative intensities of each gas in numerical format. Data was then saved on the computer's hard drive for later interpretation.

Leak Detector

A Dupont 120 SSA-leak detector mass spectrometer fitted with a special inlet system designed by the USGS, Denver was used to measure He contents [Reimer and Denton, 1976]. The mass spectrometer's detectors were tuned to the mass of ^4He and had an uncertainty of ± 10 ppb. A liquid nitrogen charcoal trap was used to extract the condensible gases.

Data was manipulated by a Hewlett-Packard computer which was linked directly to the leak-detector. The computer referenced the sample being analyzed with known standards and reported the concentrations in ppb.

RESULTS

The tables in Appendix II give soil gas CO₂ values normalized to atmosphere (332 ppm). Initially, soil gas samples were collected using a spacing of 0.25 mi. To improve resolution, a sample interval of 0.10 mi was subsequently chosen for the remainder of this study.

Samples collected in vacutainer brand glass vials and analyzed by gas chromatography produced erratic and irreproducible results. An air sample was collected in the field so that a comparison could be made between soil gas CO₂ concentrations and CO₂ in air. It became apparent that the analyses were grossly in error. Global averages for atmospheric CO₂ concentrations range from 300 to 500 ppm [Bremner and Blackmer, 1982]. The samples analyzed on the GC showed the concentration of CO₂ in air to be in excess of 2000 ppm.

Fortunately the same problem was encountered by Terhune and Harden [1991] while using vacutainers to collect soil gas samples in southern Nevada. The researchers recorded a background CO₂ level of 600 ppm within their vacutainers direct from the factory. Due to the excess CO₂ problem associated with the vacutainers, their use was discontinued. Subsequently, all soil gas samples were collected in stainless-steel cylinders.

Profiles of soil gas concentrations were constructed for each sample event. Soil gas levels vary between sample dates. The first set of gases collected at a 0.25 mi sample interval are

shown in Figure 11. The data display extreme variability in absolute soil gas CO₂. There is no obvious pattern.

The profile lines for sampling dates 7-15-91 and 7-25-91 show peak and trough correspondance at identical stations.

Absolute soil gas CO₂ levels are not

identical, but the overall trend is the same. There is a discernible trough evident at stations 10 and 17 on both profiles. Similarly, a broad peak appears between stations 11-13.

The first set of data collected at an interval of 0.10 mi is plotted in Figure 12. The overall appearance of these two lines is very different from the previous data. Troughs are coincident at stations 18 and 22. Peaks at stations 13 and 17 are apparent on both lines while station 29 shows a trend towards increasing CO₂ values. Stations 20, 23 and 26 display high CO₂ concentration on 8-15-91 whereas low readings were recorded on 8-9-91.

Figure 13 is a profile for the sampling dates 8-22-91 and 8-29-91. Only a partial line for 8-29-91 was sampled due to collection of baseline samples the same day. A definite peak is

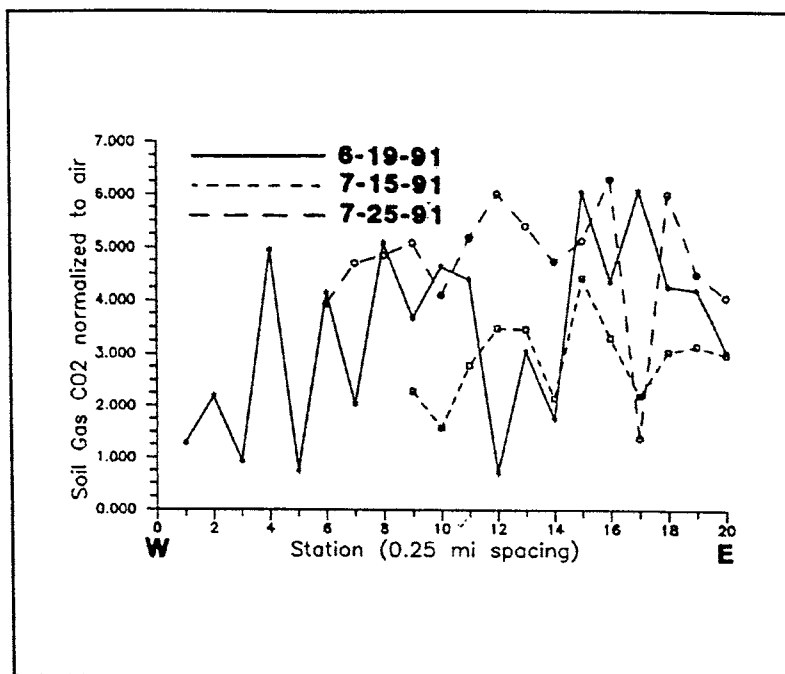


Figure 11: Soil gas CO₂ profile for Bernardo. Sample interval was 0.25 mi.

displayed at station 22. The pattern shown here for these two dates is not identical but is very similar.

The final soil gas profiles (Fig. 14) have a striking similarity which occurs at station 20. An extremely high soil gas CO₂ value of nearly 26X atmospheric level was measured on

9-19-91. Previously, the largest CO₂ value for the line sampled on 9-8-91 also occurred at station 20.

The profiles of Figure 14 show the best correlation between all the data sets collected. A composite plot of all soil gas profiles appears in Figure 15.

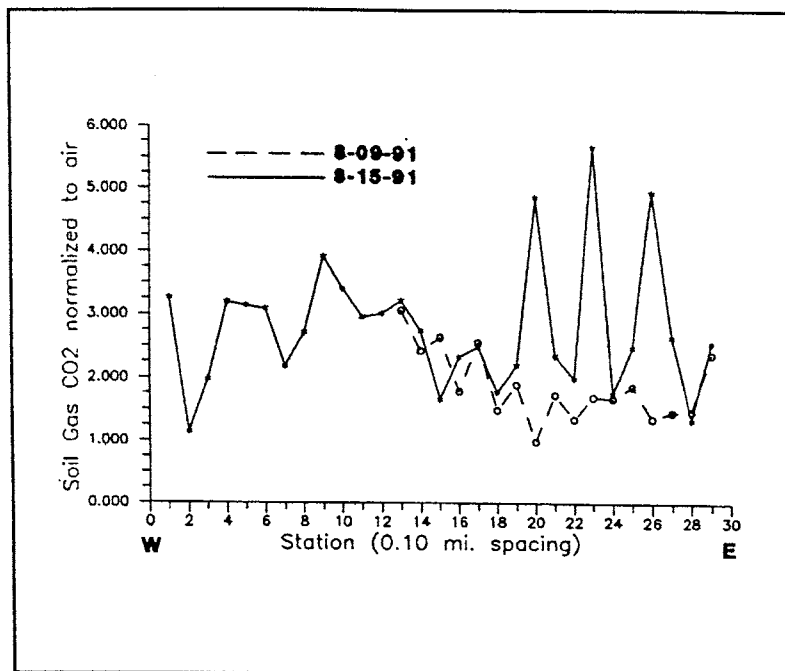


Figure 12: Soil gas CO₂ profile for Bernardo. Sample interval was 0.10 mi.

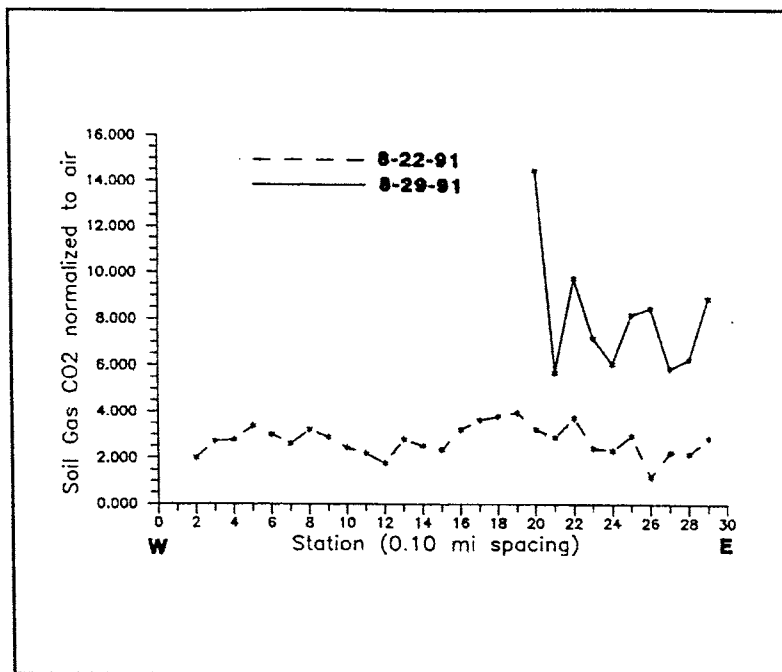


Figure 13: Soil gas CO₂ for Bernardo. Sample interval was 0.10 mi.

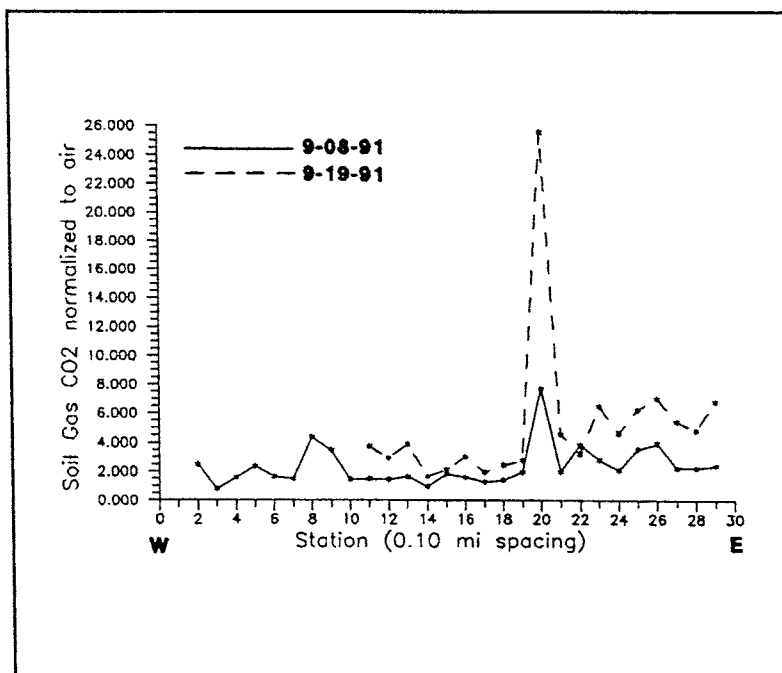


Figure 14: Soil gas CO₂ for Bernardo. Sample interval was 0.10 mi.

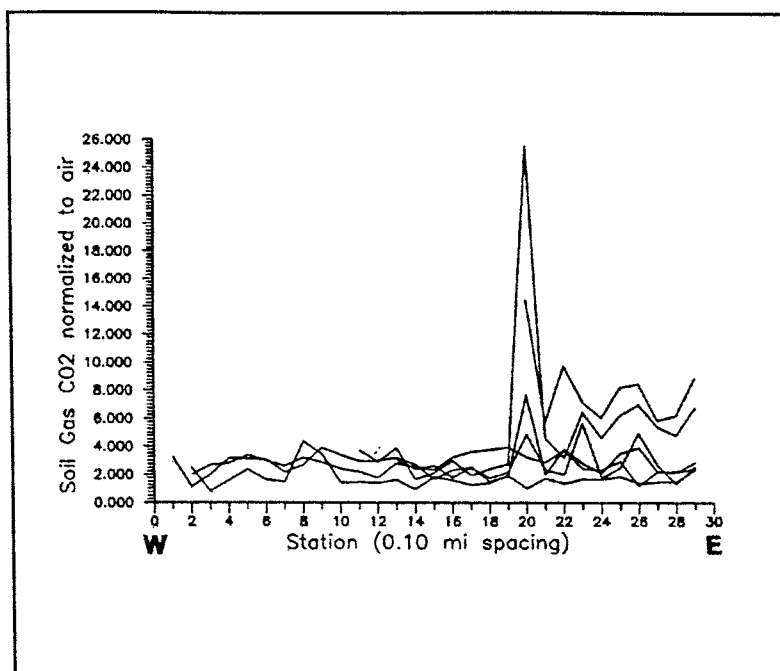


Figure 15: Composite plot of all soil gas data for Bernardo.

Baseline

The baseline profiles are shown in Figures 16 and 17. The line at San Antonio was only sampled once because of its distance from the main survey line. The Bernardo baseline was sampled twice during the project to give some indication of regional CO₂ concentrations.

The profile from San Antonio (Fig. 16) is relatively flat with soil gas CO₂ values from 4 to 19X atmosphere. Station 4 has a slightly higher value of 7.5. The soil gas CO₂ value of 18X atmosphere at station 1 appears anomalous.

The Bernardo line was sampled on 8-30-91 and 9-19-91 (Fig. 17). The two profiles are very similar in appearance. The soil gas measurements are mostly confined between values of 4 to 6X

atmosphere. Since the majority of readings occurred between 4 and 6X normal atmospheric CO₂, this range was taken to be the normal baseline for the study area. A major peak exists at station 3 where a soil gas CO₂ reading of nearly 18X

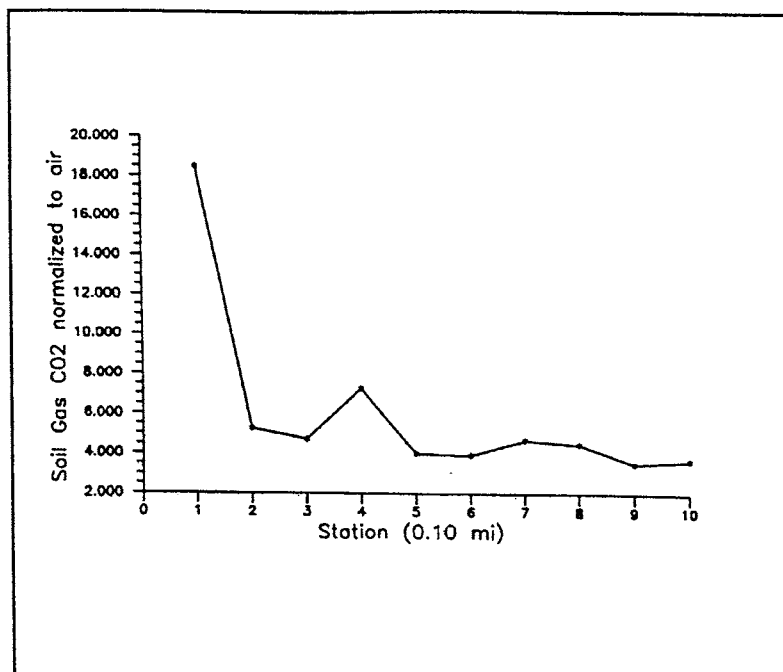


Figure 16: Soil gas CO₂ for baseline at San Antonio, New Mexico.

on 8-30-91. The

remainder of the profile is subdued with no obvious pattern.

Base station CO₂ values were recorded beginning on 7-25-91. Data was collected from a single point over a period of nearly 70 days encompassing the entire duration of the investigation (Fig. 18).

The overall pattern of soil gas CO₂ anomalies at Bernardo is not what was expected. Before the sample analyses, I had anticipated seeing soil gas profiles as bell-shaped curves. The expectation was that as CO₂ exsolved from a magma body at 4-7 km, the gas would uniformly diffuse to the surface in the shape of a large cone. The data show no supporting evidence for this claim.

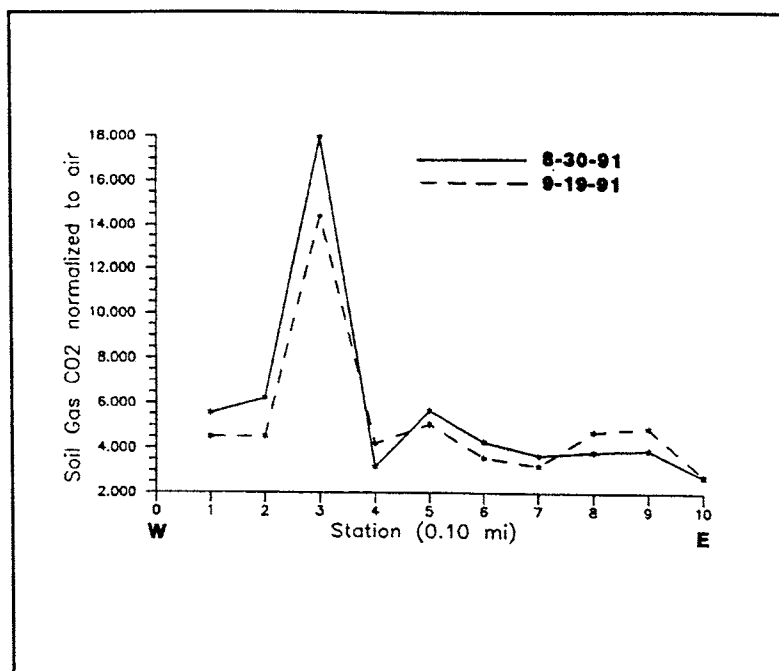


Figure 17: Soil gas CO₂ baseline at Bernardo for 8-30-91 and 9-19-91.

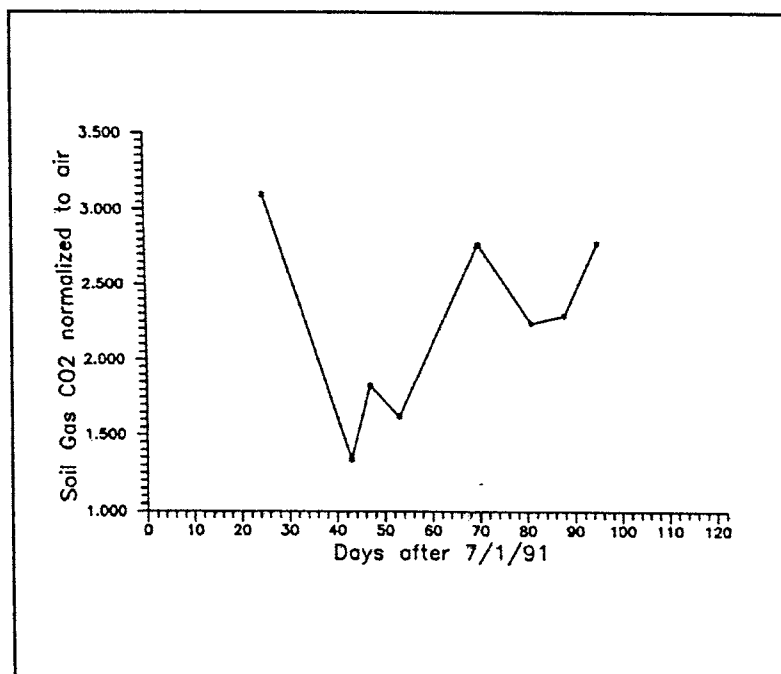


Figure 18: Soil gas CO₂ values for base station, Bernardo.

CO₂ and He Grid

As continuous data was collected, I decided to concentrate the soil gas survey in a grid around station 20 on the main survey line. Station 20 had the most consistently high soil gas CO₂ throughout the duration of the survey. This station was divided into a cross for CO₂ and He analyses (Fig. 19). Station 20 was the center of the grid. Additional samples were collected at 90° from station 20 at distances of 50 and 100 ft in all 4 directions.

A comparison between CO₂ and He in Figure 19 reveals a relationship between elevated CO₂ soil gas and high He concentrations. The center of the cross has a CO₂ concentration of 17.71X atmosphere. Helium at the same station has a concentration of 5308 ppb. This value of 5308 ppb is the second highest He value next to 5310 ppb just 50' south of station 20. The greatest He reading (5310 ppb) is also an area of high CO₂ at 16.79X atmosphere.

Some points on the cross show an inverse correlation between soil gas CO₂ and He. The point 150' north of station 20 has a CO₂ concentration of 9.69X atmosphere. Helium at the same point has a concentration of 5248 ppb. The CO₂ reading of 9.69 is the third highest CO₂ measurement whereas the He value of 5248 ppb is the seventh largest He concentration. This observation does not support a direct correlation between high soil gas CO₂ and anomalous soil gas He.

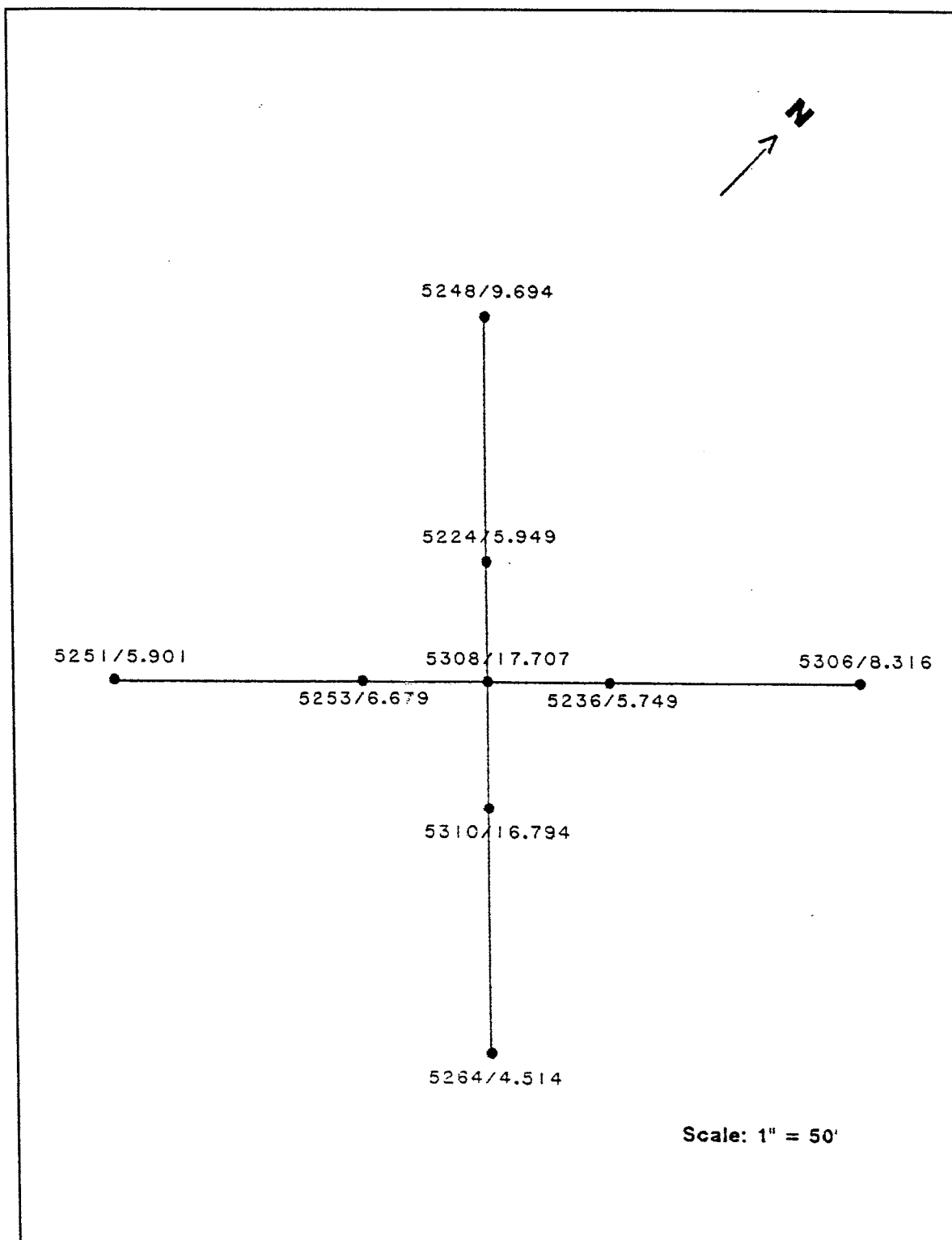


Figure 19: He and CO₂ values (He/CO₂) around station 20, main survey line, Bernardo.

Climatological Factors Affecting Soil Gas Concentrations

Weather data for the period from 7/1/91 to 10/30/91 was obtained to determine what effect if any climatological factors had on observed soil gas values. Graphs of daily precipitation, soil temperature, air temperature, wind speed, vapor pressure, and relative humidity are shown in Figures 20-25.

The soil and air temperatures (Figs. 21, 22) show a similar pattern to each other as do vapor pressure and relative humidity (Figs. 24, 25). Precipitation occurred mainly during the monsoon season in the months of July, August, and September (Fig. 20). The wind speed plot (Fig. 23) shows no obvious pattern.

Comparison of these plots to observed soil gas concentrations showed that only precipitation affected the soil gas measurements (Fig. 26). The first soil gas data point, appearing at the 25 day mark, has a concentration of 3.25X atmosphere. This value was recorded 4 days after a period in which over 12 mm of

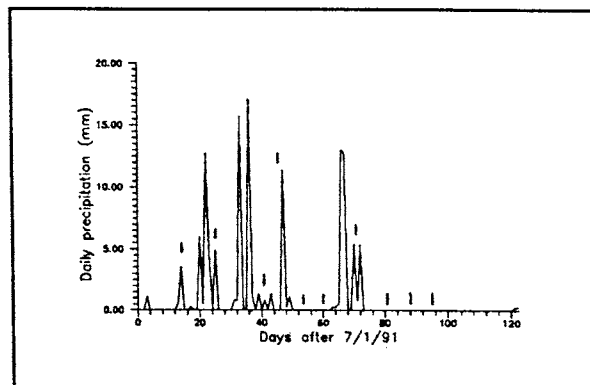


Figure 20: Average daily precipitation for the area near Bernardo. Tick marks show dates of sample collection.

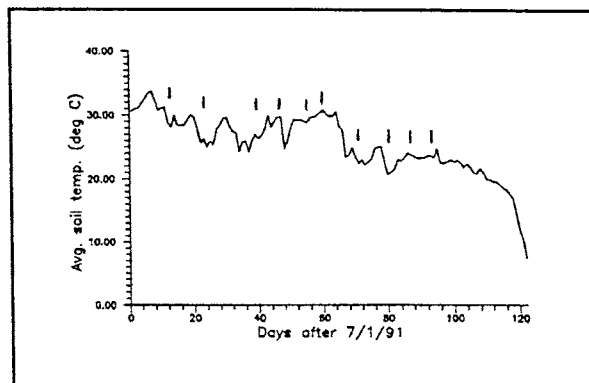


Figure 21: Average maximum daily soil temperature for Bernardo.

precipitation had occurred. The second data point, at the 44 day mark, is situated in an interval where no substantial precipitation had been recorded for nearly a week. The remaining data points all show similar correlations between antecedent precipitation and increased soil gas concentrations. Low values of soil CO₂ occurred during times of little or no precipitation. No correlation is apparent near the 8th data point where a higher than expected soil gas value exists without a previous period of intense rainfall. This anomalous CO₂ value may be the result of increased biological activity within the soil due to the preceding weeks of precipitation.

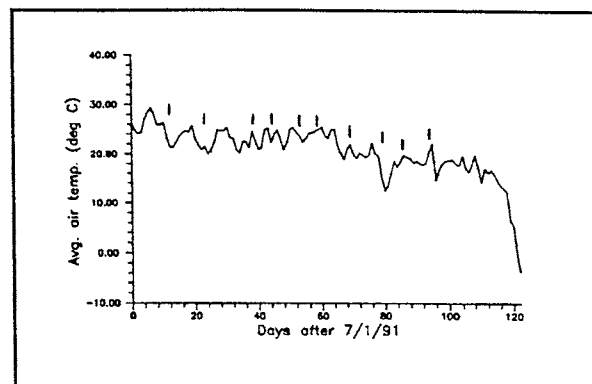


Figure 22: Average maximum daily air temperature for Bernardo.

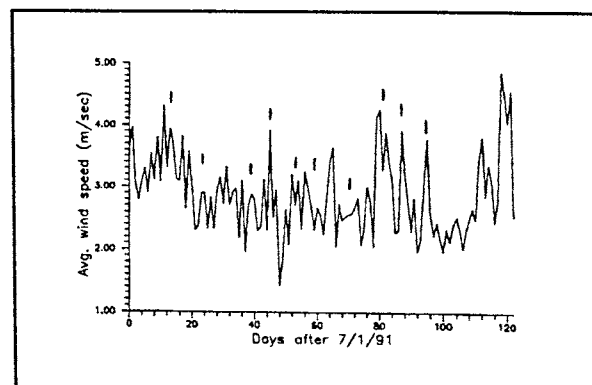


Figure 23: Average maximum daily wind speed for Bernardo.

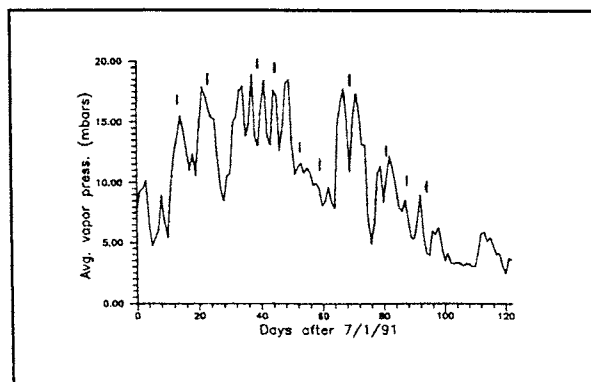


Figure 24: Average daily vapor pressure for Bernardo.

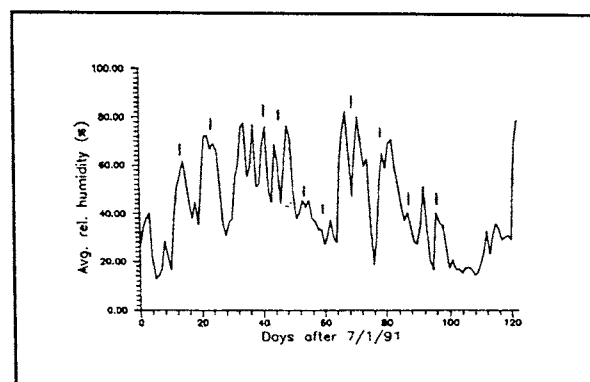


Figure 25: Average relative humidity for Bernardo.

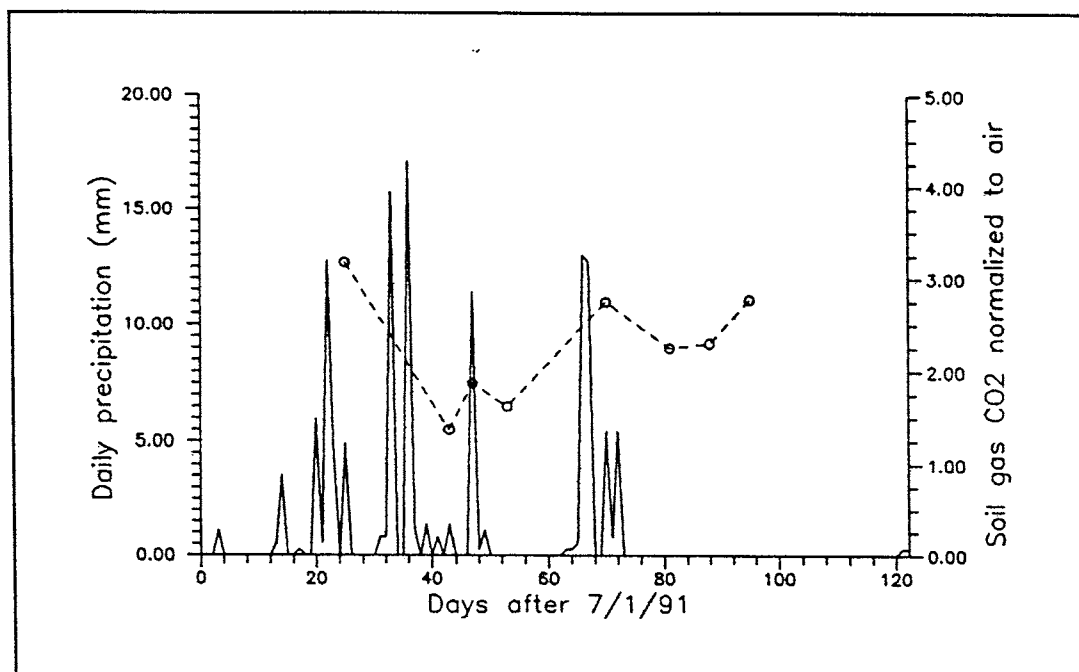


Figure 26: Plot of soil gas CO₂ relative to daily precipitation for Bernardo.

DISCUSSION

The soil gas profiles all show variability between sample intervals. This variability is most likely the result of changes in soil moisture between sampling events. High levels of soil gas CO₂ appear to have been influenced by daily precipitation. Other climatological factors such as wind speed and soil temperature may have affected soil gas measurements to some degree. Biological activity in the soil may also be a contributing factor to variable soil gas CO₂.

The reproducibility of the data is apparent when looking at the baseline profile for Bernardo. The general pattern observed on 8-30-91 was reproduced by sampling on 9-19-91. This proves the validity of the sampling procedure and analytical work. The encouraging argument here is that the variability in soil gas CO₂ displayed in the main sample line is not an artifact of incorrect field procedure or questionable laboratory technique.

The baselines at Bernardo and San Antonio aided in establishing the normal background soil gas concentrations for central New Mexico. Soil gas profiles constructed from the baseline data were mostly flat. An occasional measurement would be higher than the average soil gas value for a particular line. These measurements were not representative of the entire line.

Soil gas measurements on the main survey line showed extreme variability between stations spatially as well as temporally. The profiles for normal baselines and the main survey line are very different in appearance. This suggests different sources for the

gases of the main line compared with those of normal background. Anomalous soil gas near the most recent seismicity at Bernardo may be originating from shallow magma bodies at 4-7 km and migrating to the atmosphere through a complex fracture network.

Anomalous soil gas CO₂ readings were not always associated with high He values. A direct correlation between these two gases would seem justified if they both had similar origins. An alternative explanation for a lack of correlation between these two gases is due to displacement. If CO₂ concentrations are much greater than He, the CO₂ may displace He from the soil. This would result in an inverse relationship between CO₂ and He concentrations in soils.

CONCLUSIONS

The soil gas investigation near Bernardo defined areas of anomalous CO₂ and He. The absolute values of these anomalies varied between sampling intervals due to climatic factors such as soil moisture.

The location of soil gas anomalies is near but does not coincide directly with the most recent seismicity. This may be due to errors in locating earthquake epicenters or the preferential migration of gases through fracture networks. Exsolved gases may be moving to the surface in a "honey comb" fashion. Rather than migrating in a single coherent form, the gases may bifurcate and diffuse as an interconnected gas network.

To better understand the nature of soil gas anomalies in this region, permanent monitoring stations should be established and periodically sampled. The likelihood of sampling soil gases during a seismic event will be greatly increased.

In addition to permanent monitoring, samples should be collected for carbon and helium isotope analyses to better understand the origin of the anomalous soil gases.

APPENDIX I

TABLE I CO₂ Emission Rates for Subaerial Volcanoes*

<u>Volcano</u>	<u>Geologic Setting</u>	<u>Rate (10¹² mol/yr)</u>
Mount St. Helens Cascades, Western U.S.	convergent plate dacitic magma	0.04
White Island New Zealand	convergent plate andesitic magma	0.03
Augustine Alaska	convergent plate andesitic/dacitic	0.0073
Vulcano Aeolian Islands	convergent plate trachyandesitic	0.0015
Redoubt Alaska	convergent plate andesitic	0.015
Mount Etna Sicily	intra-plate alkalic basalt	0.58
Kilauea Hawaii	intra-plate tholeiitic basalt	0.03

* Modified from Gerlach, 1991

APPENDIX II

The PASCAL program Solubility was developed to calculate the amount of CO₂ exsolved from a basaltic magma due to decreasing pressure. The following algorithm used for the computation was developed by Holloway (1991) and is accurate to within 5%.

$$\text{wt\%CO}_2 = 0.00119 + 4.81438 \times 10^{-5}(P) + 5.019505 \times 10^{-9}(P^2) \\ - 2.587138 \times 10^{-13}(P^3) + 5.96362 \times 10^{-18}(P^4) - 5.67816 \times 10^{-23}(P^5)$$

The algorithm assumes tholeiitic composition and is valid for a pressure range of 30-200 kbars.

Program Solubility; {This program calculates the weight percent CO2 in magma under a pressure 'P' in bars}

Uses crt;

Var

```

    PH : real;  {higher pressure}
    PL : real;  {lower pressure}
    PHZ : real; {greater depth}
    PLZ : real; {lesser depth}
    Ans : char;
    Ex  : real;  {wt% CO2 exsolved: WtPerH - WtPerL}

```

Function WtPerH (PH: real) : real; {Function calculates the wt% CO2 in a magma at pressure 'P'}

```

begin
    WtPerH := ((0.00119 + (0.0000481438 * PH)) +
               (0.000000005019505 * (exp(2 * ln(PH)))) -
               (0.00000000000002587138 * (exp(3 * ln (PH)))) +
               (0.000000000000000000596362 * (exp(4 * ln(PH)))) -
               (0.0000000000000000000000567816 * (exp(5 * ln(PH)))))
end;

```

Function WtPerL (PL: real) : real;

```

begin
    WtPerL := ((0.00119 + (0.0000481438 * PL)) +
               (0.000000005019505 * (exp(2 * ln(PL)))) -
               (0.00000000000002587138 * (exp(3 * ln (PL)))) +
               (0.000000000000000000596362 * (exp(4 * ln(PL)))) -
               (0.0000000000000000000000567816 * (exp(5 * ln(PL)))))
end;

```

Begin {MAIN}

ClrScr;

Writeln;

Writeln('

This program calculates the weight percent CO2 exsolved');

Writeln('

from a tholeiitic magma as it ascends buoyantly through');

Writeln('

the earth's crust.');

Writeln;

Writeln('

Begin by entering the initial depth of the diapir, in kilometers,');

Writeln('

followed by its final depth, (at isostatic equilibrium).');

Writeln;

repeat

Writeln;

Writeln;

Writeln;

```
Write('Enter initial depth in kilometers: ');
Readln(PHZ);
Writeln;
PH := ((PHZ) * 380);
Write('Enter final depth in kilometers: ');
Readln(PLZ);
PL := ((PLZ) * 380);
Writeln;
  if (PH > 0) and (PL > 0)
  then begin
    Writeln('The CO2 solubility at ', PHZ:2:2, '
kilometers is: ', WtPerH(PH):2:6, ' wt%');
    Writeln;
    Writeln('The CO2 solubility at ', PLZ:2:2, '
kilometers is : ', WtPerL(PL):2:6, ' wt%');
    Ex := WtPerH(PH) - WtPerL(PL);
    Writeln;
    Writeln('The amount of CO2 exsolved is:
', Ex:2:6, ' wt%')
  end
  else begin
    Writeln('Please use a non-zero pressure!');
    Writeln
  end;
Writeln;
Write('Would you like to do another (Y/N) ? ');
Readln(Ans);
ClrScr
until UpCase(Ans) = 'N'
```

End.

APPENDIX III

TABLE II

CO₂ Soil Gas Concentrations at Bernardo, New Mexico; Relative to Atmosphere
(concentration/concentration_{air})
(0.25 mi spacing)

Station #	6-19-91	7-15-91	7-25-91
1	---	1.283	---
2	---	2.192	---
3	---	0.933	---
4	---	4.955	---
5	---	0.757	---
6	3.939	4.150	---
7	4.706	2.046	---
8	4.853	5.089	---
9	5.091	3.671	2.291
10	4.111	4.652	1.581
11	5.192	4.400	2.784
12	6.022	0.722	3.484
13	5.418	3.061	3.469
14	4.744	1.763	2.157
15	5.139	6.072	4.431
16	6.313	4.374	---
17	1.389	6.099	2.207
18	6.022	4.275	3.052
19	4.503	4.207	3.153
20	4.069	3.059	2.993

TABLE II (continued)

CO ₂ Soil Gas Concentrations at Bernardo, New Mexico; Relative to Atmosphere (concentration/concentration _{air}) (0.10 mi spacing)						
Station #	8-9-91	8-15-91	8-22-91	8-29-91	9-8-91	9-19-91
1	---	3.254	---	---	---	---
2	---	1.137	1.998	---	2.495	---
3	---	1.975	2.719	---	0.790	---
4	---	3.191	2.794	---	1.576	---
5	---	---	3.380	---	2.375	---
6	---	3.083	3.014	---	1.640	---
7	---	2.179	2.626	---	1.488	---
8	---	2.712	3.223	---	4.355	---
9	---	3.918	2.893	---	3.469	---
10	---	3.405	2.432	---	1.423	---
11	---	2.956	2.190	---	1.486	3.739
12	---	3.014	1.770	---	1.422	2.920
13	3.060	3.216	2.800	---	1.636	3.884
14	2.421	2.740	2.520	---	0.945	1.652
15	2.642	1.660	2.353	---	1.834	2.132
16	1.791	2.332	3.229	---	1.588	3.015
17	2.561	2.490	3.638	---	1.262	1.944
18	1.494	1.782	3.800	---	1.398	2.437
19	1.900	2.208	3.958	---	1.962	2.772
20	0.996	4.866	3.247	14.468	7.692	25.577
21	1.742	2.358	2.895	5.687	1.977	4.564
22	1.356	2.006	3.748	9.753	3.836	3.221
23	1.702	5.675	2.412	7.181	2.803	6.462
24	1.681	1.765	2.325	6.067	2.093	4.612
25	1.878	2.495	2.967	8.183	3.529	6.233
26	1.367	4.955	1.184	8.482	3.941	6.997
27	1.472	2.662	2.249	5.873	2.217	5.409
28	1.484	1.342	2.185	6.260	2.234	4.798
29	2.391	2.572	2.872	8.898	2.398	6.775

TABLE III

Date	Base-station CO ₂ Concentrations Soil gas CO ₂ relative to air (concentration/concentration _{air})
7/25/91	3.097
8/09/91	1.335
8/15/91	1.828
8/22/91	1.619
9/08/91	2.769
9/19/91	2.239
9/26/91	2.293
10/03/91	2.775

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