

SOIL GAS $\delta^{13}\text{C}$ VALUES AND CO_2 CONCENTRATIONS ON THE SOUTHEAST
SLOPE OF MAUNA KEA:
IMPLICATIONS FOR PALAEOCLIMATE AND HYDROGEOLOGY

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAI'I IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

GEOLOGY AND GEOPHYSICS

AUGUST 2004

By

Elaine R. Smid

Thesis Committee:

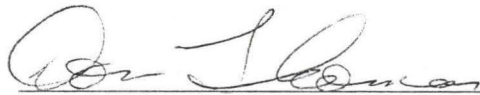
Donald M. Thomas, Chairperson

Brian Popp

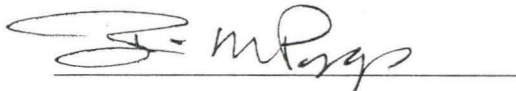
Fred Mackenzie

We certify that we have read this thesis and that, in our opinion, it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Geology and Geophysics.

THESIS COMMITTEE

A handwritten signature in cursive script, appearing to read "Don Thomas", written over a horizontal line.

Chairperson

A handwritten signature in cursive script, appearing to read "J. M. P.", written over a horizontal line.A handwritten signature in cursive script, appearing to read "A. M. P.", written over a horizontal line.

ACKNOWLEDGMENTS

I would like to acknowledge the National Science Foundation for providing financial support for this project.

I am grateful to Drs. Fred Mackenzie and Brian Popp for their insight and expertise, for serving as my committee members, and for reviewing thesis manuscripts. Dr. Jane Schoonmaker generously volunteered her time and expertise as a potential proxy member of my committee during my oral defense. Many thanks go to her for stepping in so willingly. I am especially grateful to Dr. Donald Thomas, my advisor, for his endless support and for our discussions.

I am eternally grateful to Dave Whilldin for lending his GPS, driving, and hiking expertise and for keeping field work enjoyable and interesting. The fieldwork would have been practically impossible without him.

I would like to thank Terri Rust for her time, good humor, endless patience, and for sharing her vast GC-MS knowledge with me as I learned how to use the 252 and analyze the data.

Thanks go out to Aisha Morris, Todd Bianco, and Julia Sable for their assistance during various sampling trips and for their friendship. Nancy Adams and Jonathan Weiss were also sources of constant support during this project. I thank you all and the rest of my family in Hawai'i for making my time here so wonderful.

Finally, I would like to thank all of the GG faculty and graduate students, as well as my family and friends on the mainland, for their support during my project.

ABSTRACT

As part of the Hawai'i Scientific Drilling Project (HSDP), an elevational transect on the southeast slope of Mauna Kea Volcano, Hawai'i, was sampled for soil gas CO_2 $\delta^{13}\text{C}$ over a one-year study interval. Our objective is to determine the principle influences on the $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) that is contributed to groundwater recharged in the area. Groundwater DIC from the HSDP drill hole, dated to 2200 B.P., had a carbon isotopic value of -12‰. The $\delta\text{D}/\text{H}$ and $\delta^{18}\text{O}$ values of the water indicate that the average elevation of recharge is at 2000 m on Mauna Kea. It was postulated that this $\delta^{13}\text{C}$ was controlled mainly by the photosynthetic pathway of the predominant vegetation at this elevation at the time of recharge. If this is true, the current $\delta^{13}\text{C}$ values should have changed as a result of the conversion of the formerly forested Mauna Kea slopes to grassland in the past 2200 years.

Results support this hypothesis. Present day $\delta^{13}\text{C}$ values range from -12‰ in grasslands at 2000 m ASL to -24‰ in the lower elevation forested areas. With the soil gas values of -12‰ in the grasslands, fractionation between soil gas and bicarbonate in groundwater would cause the DIC in groundwater to have values of -3‰ today. The conversion of this area to grassland approximately 200 years ago and the introduction of exotic C_4 grasses are assumed to be the causes of the difference, as C_3 trees have lighter values than C_4 grasses.

Other areas of the transect follow predicted patterns for vegetation type. There

was a slight decrease in ^{13}C content from summer to winter, which is opposite of expected seasonal trends. This lighter value could be due to the very dry conditions in the winter (due to El Niño) or cool-season grasses taking over in production in the winter. In diurnal samples, daytime $\delta^{13}\text{C}$ values were a few per mille lighter than nocturnal values. Samples taken in recently burned areas showed similar $\delta^{13}\text{C}$ values but lower CO_2 concentrations. The values can be divided into two groups, which follow the major photosynthetic pathways of the area. The lower 4 forested areas show no difference in values, but the upper two pasture lands show some difference, which is attributed to a greater proportion of C_4 grasses in the lower elevation pasture.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	iii
ABSTRACT.....	iv
LIST OF TABLES.....	viii
LIST OF FIGURES.....	ix
CHAPTER 1: INTRODUCTION TO THE PROJECT.....	1
1.1 BACKGROUND.....	1
1.2 HYPOTHESIS.....	4
CHAPTER 2: CO ₂ CONCENTRATIONS AND δ ¹³ C VALUES IN NATURAL SYSTEMS.....	6
2.1 THE CARBON CYCLE.....	6
2.2 CARBON ISOTOPE VALUES.....	8
Natural Ranges of δ ¹³ C Values.....	9
2.3 OCEAN-ATMOSPHERE-SOIL-GROUNDWATER-GEOLOGY SYSTEMS.....	9
Ocean-Atmosphere System.....	10
Atmosphere-Soil and Atmosphere-Plant Systems.....	11
<i>Atmospheric CO₂ Concentrations and δ¹³C Values</i>	12
<i>Atmosphere-Soil System</i>	15
<i>Soil Respiration</i>	16
<i>Canopy enrichment</i>	18
<i>Volcanic Sources</i>	19
<i>Atmosphere-Plant</i>	20
<i>Microbial Respiration</i>	20
<i>Root Respiration</i>	21
<i>Vegetation</i>	22
<i>Environmental conditions and metabolic pathways</i>	27
<i>Root vs. Microbial Respiration</i>	29
<i>CO₂ Concentrations and δ¹³C Values in Soil Gas</i>	30
<i>δ¹³C values of soil gas CO₂</i>	31
<i>Diurnal variations in δ¹³C values</i>	32
<i>Seasonal variations in δ¹³C values</i>	33
<i>The Effect of Temperature and Moisture</i>	33
Soil-Groundwater System.....	35
Groundwater-Geology System.....	38

CHAPTER 3: SITE DESCRIPTION, METHODS, AND MATERIALS.....	41
3.1 GENERAL SITE DESCRIPTION.....	41
3.2 VISITS, TRIPS, AND NUMERATION.....	48
Rainfall in the transect.....	50
3.3 AREAS AND SITES OF THE TRANSECT.....	50
Area 1.....	50
Area 2.....	53
Area 3.....	54
Area 4.....	56
Area 5.....	56
Area 6.....	57
Non-transect areas.....	57
<i>Western Mauna Kea--Area 7.....</i>	<i>58</i>
<i>Oahu--Area 8.....</i>	<i>58</i>
Diurnal/Nocturnal Samples.....	58
Vegetation Samples.....	59
Soil samples.....	59
3.4 MATERIALS AND METHODS.....	59
Vegetation Samples.....	63
Soil samples.....	63
Calculation of the $\delta^{13}\text{C}$ value of DIC.....	63
 CHAPTER 4: RESULTS AND DISCUSSION.....	 67
4.1 TRENDS IN $\delta^{13}\text{C}$ VALUES WITH ELEVATION.....	67
The Source of the Two Populations.....	68
Trends Within the Two Populations.....	71
4.2 SEASONAL TRENDS IN $\delta^{13}\text{C}$ VALUES.....	76
4.3 $\delta^{13}\text{C}$ VALUES AND CO_2 CONCENTRATIONS WITH DEPTH.....	80
4.4 DIURNAL/NOCTURNAL $\delta^{13}\text{C}$ VALUES AND CO_2	
CONCENTRATIONS.....	83
4.5 RECHARGE ZONE SOIL GAS $\delta^{13}\text{C}$ VALUES AND ECOSYSTEM	
CHANGE.....	86
4.6 FUTURE WORK.....	91
 REFERENCES.....	 92

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Average annual temperature at elevations used in this study.....	44

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Carbon fluxes and reservoirs.....	7
2. Atmospheric CO ₂ with time.....	13
3. Atmospheric δ ¹³ C values from 2002 to 2004 at Mauna Loa Observatory.....	15
4. Distribution of carbon species as fraction of total carbon dissolved in water with pH at 25 °C.....	37
5. Ranges of ¹³ C values of various substances.....	38
6. Maps of transect areas.....	43
7. How δ ¹³ C values of DIC would change with varying amounts of C ₄ plant ground cover and atmospheric mixing	46
8. Schematic of soil gas sampling set up.....	58
9. δ ¹³ C values with elevation from all sampling periods on Mauna Kea.....	68
10. Average δ ¹³ C values with elevation at each area with season.....	76
11. Average δ ¹³ C values with time of year.....	80
12. CO ₂ concentrations with depth.....	82
13. δ ¹³ C values with time.....	86

CHAPTER 1

INTRODUCTION TO THE PROJECT

1.1 BACKGROUND

Deforestation and fossil fuel combustion are increasing the CO₂ content of the atmosphere every year, and greater amounts of CO₂ in the atmosphere are linked to increases in temperature due to the heat trapping, radiative properties of CO₂ (Clark 1982). Continuing increases in global average temperature may further upset the carbon balance and cause positive feedback reactions that could expedite climate change. Past climate changes have been linked to the carbon content in the atmosphere and serve as an outline to the changes we may expect (Barnola 1987; Appenzeller 1992). Because the rate of increase in atmospheric CO₂ and other greenhouse gases is unprecedented, it may produce results that have not been encountered previously (Kasting 1998). As a result, the focus of much recent research in climate science has been on quantifying the various fluxes and pools in the carbon cycle. One of the main goals is to balance the carbon budget and better understand the changes occurring in the C-cycle so the future climate may be accurately modeled (Kerr 1992; Wofsy 2001).

A disturbing, major unknown in climate science today is the response of soils and their vast stores of carbon to global warming (Schlesinger 2000). Containing three to four times more carbon than currently exists in the atmosphere (Stevenson 1999), the increased release or storage of carbon in soils could either intensify or alleviate the effect of human-induced CO₂ changes (Rustad 2000). Given the recent debates concerning the

effect of increased CO₂ on earth systems, and especially the uncertain role of soils in these scenarios, further investigations are necessary to be able to predict future CO₂ changes and the human impact on biogeochemical cycles more accurately (Giardina 2000; Schubler 2000). $\delta^{13}\text{C}$ values, which are based on the relative amount of ¹²C to ¹³C, are one way to examine CO₂ dynamics, and are used in this study.

The effect that deforestation has on local and global moisture patterns can be disturbing. The conversion of forestland to pasture has proven to drastically change rainfall patterns and infiltration dynamics in an area (Meher-Homji 1989; Salati 1991; Ravindranath 1998). This, in turn, may affect the amount of recharge to aquifers below that land (Bruijnzeel 1986; Ravindranath 1998). Communities that rely on groundwater resources, or even aboveground rain catchments, may be negatively impacted by deforestation. Therefore, the effect of clearing land and changing vegetation in an area has far-reaching consequences. On islands especially, water quality and availability are critical issues (Anthony 1993). Understanding the factors that influence them is especially important as the population and consequent demand for water grows.

The Hawai'i Scientific Drilling Project (HSDP) is an on-going, multi-objective venture intended to understand, in part, the hydrogeology of oceanic island systems. A freshwater aquifer located approximately 320 m below sea level was discovered in HSDP's one-kilometer deep pilot borehole Kahi Puka 1 (KP-1) on the Island of Hawai'i (Thomas 1996). This aquifer is estimated to recharge at approximately 2000 m elevation on the southeastern slopes of Mauna Kea Volcano, Hawai'i. Dissolved inorganic carbon

(DIC) in this groundwater below the drillsite was dated to 2200 years B.P. and had an average $\delta^{13}\text{C}$ value of -12‰. At equilibrium, a $\delta^{13}\text{C}$ value of -12‰ in DIC is indicative of a soil gas $\delta^{13}\text{C}$ value of approximately \sim -21‰ at a temperature of 11.6 °C (from mean annual temperature calculations and a pH of 7.8 (taken from the pH of borehole sample water)). The goals of this project were to determine the primary source for $\delta^{13}\text{C}$ values in this region, determine if and why the $\delta^{13}\text{C}$ values had changed in the past 2200 years, and to define soil CO_2 and $\delta^{13}\text{C}$ trends: 1) with depth in the soil, 2) along an altitudinal transect, and 3) diurnally and seasonally (rainy/dry seasons) in the recharge zone on Mauna Kea Volcano, Hawai‘i, in order to elucidate the controlling factors contributing to $\delta^{13}\text{C}$ values in Hawaiian aquifers.

More carbon is exchanged annually with the atmosphere in the tropics than in any other region (Box 1988). The tropics are also the site of a greater percent of land use changes, often leading to the addition of more carbon to the atmosphere (Davidson 1993). There are few previous studies investigating the carbon isotopes of soil gas CO_2 in the tropics, and studies examining tropical soil gas $\delta^{13}\text{C}$ values along altitudinal and depth transects with time of day and season are rare (Townsend 1997; Amundson 1998). Hawai‘i’s unique geographic position and environment provides a non-biased setting for examining CO_2 dynamics in soil systems. A continuous measurement of CO_2 levels and other atmospheric gases are recorded at \sim 3300 m elevation on the flanks of Mauna Loa Volcano on the Island of Hawai‘i in part due to Hawai‘i’s location far from large cities and other anthropogenic sources of CO_2 (Keeling 1982; Keeling 2002).

Chapter 1 of this thesis introduces the topic of the project, its importance, and the results expected from this study. Chapter 2 describes how CO₂ concentrations and δ¹³C values change as carbon moves from the atmosphere into the plant or soil systems to the groundwater system. Chapter 3 details the materials, methods, and instrumentation used in the implementation of this project and provides detailed site descriptions. Finally, Chapter 4 presents the results of analyses of vegetation, soil, and soil gas CO₂ samples collected diurnally and seasonally along the soil depth and altitude transect, discusses the conclusions made from the results of this study, and closes the thesis by outlining further work that needs to be done in this field.

1.2 HYPOTHESES

This experiment is testing the hypothesis that δ¹³C values of soil gas in the recharge zone today will be different from the δ¹³C values of soil gas corresponding to the 2200 year old groundwater on the Island of Hawai'i. This will be due to vegetation and climate changes since the time of recharge. The current variations found within the transect will primarily be due to vegetation differences. Concentrations of CO₂ and δ¹³C values will vary with depth, elevation, and vegetation, and therefore, climate of the area. More negative δ¹³C values will correspond to soils vegetated by C₃ plants, which discriminate against δ¹³C to a greater degree than C₄ plants. The atmospheric contribution to soil gas CO₂ will be minor, with concomitant decreases at progressively greater depths and with increasing moisture levels. Volcanic CO₂ is expected to be an

even less significant factor, as Mauna Kea completed its main period of vigorous activity, or shield-building stage, ~70 ka (Wolfe 1997). Microbially produced, root respired, and atmospheric CO₂ will all vary seasonally and diurnally, following moisture levels and temperature patterns. Following previous studies, the most enriched $\delta^{13}\text{C}$ values and lowest CO₂ contents in the soils are predicted during the day, while the most depleted values and highest CO₂ concentrations are expected to occur just before dawn (Huck 1962; Dudziak 1996).

No changes in $\delta^{13}\text{C}$ values are expected to occur in transit from the recharge zone to the borehole due to reactions within the aquifer, e.g. sulfate reduction (no sulfide was found in the borehole waters) or methanogenesis (no evidence of anaerobic, reducing conditions exists) (Thomas 2004). Therefore, the $\delta^{13}\text{C}_{\text{DIC}}$ value of the water entering the aquifer system at the recharge zone will be the value of the water exiting the borehole.

CHAPTER 2 CO₂ CONCENTRATIONS AND δ¹³C VALUES IN NATURAL SYSTEMS

2.1 THE CARBON CYCLE

Carbon is found in virtually every medium and in many forms—organic, inorganic, dissolved, gaseous, and in rocks, in the ocean, within organisms, in fossil fuels, in the atmosphere, and within soils (Rustad 2000). Some of these pools are absorbing and storing carbon (sinks), while others are releasing it (sources). The amount of available carbon at any time is a function of the rates of cycling among the various pools, and affects the radiative properties of the atmosphere. A vast majority of carbon on Earth is stored in sedimentary rocks for long periods of time; however, this carbon does not play an active role on short, centennial time scales (Figure 1). The main short-term active reservoir of carbon on land is in the soil, holding 3000 to 5000 gigatons (Gt) of carbon (Stevenson 1999).

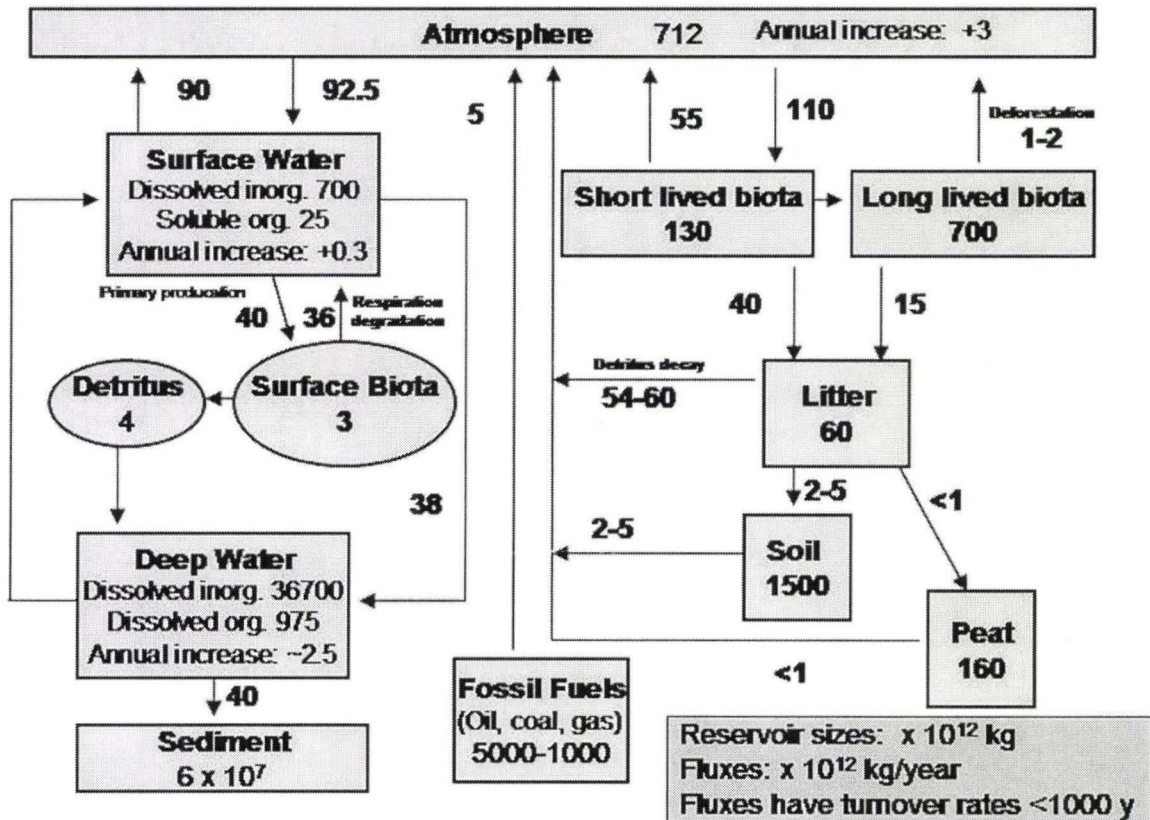


Figure 1. Carbon Cycle Fluxes and Reservoirs. Numbers beside arrows are fluxes (10^{12} kg/year) and reservoir sizes are listed inside boxes (10^{12} kg). Arrows indicate the direction of carbon fluxes. The soil reservoir is the largest short-term reservoir (recreated from Stevenson, 1999).

2.2 CARBON ISOTOPE VALUES

Carbon has two stable isotopes, ^{12}C and ^{13}C ; the vast majority of carbon is in the form of ^{12}C , but a small fraction is found as ^{13}C . Minute differences in the mass (8.3%) and chemistry of these two isotopes allow one or the other to become concentrated during natural processes (O'Leary 1981). For example, plants take up ^{12}C , the lighter isotope, preferentially over ^{13}C due to biochemical processes within the plant. The atmosphere then becomes relatively enriched in ^{13}C while the plant tissue will contain more ^{12}C ; the degree of separation (fractionation) will depend on the plant type, temperature, moisture availability, CO_2 concentration, and many other factors.

In order to compare substances to one another, the ratio of ^{13}C to ^{12}C is normalized using the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in CO_2 extracted from a universal standard. This $\delta^{13}\text{C}$ value reveals if the substance is enriched or depleted in ^{13}C compared to the standard. In the past, the universal standard was a marine limestone, Vienna PeeDee Belemnite, or V-PDB (O'Leary 1988). Currently, the diminished resources of V-PDB require the use of secondary or tertiary standards, previously referenced against V-PDB (Fry 1989). The ratios are converted to $\delta^{13}\text{C}$ using the following equation:

Eq. 1:
$$\delta^{13}\text{C} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) * 1000$$

where $R = ^{13}\text{C}/^{12}\text{C}$. Units are in per mille (parts per thousand), or ‰.

V-PDB has a $\delta^{13}\text{C}$ defined as 0‰ and a $^{13}\text{C}/^{12}\text{C}$ ratio of 0.0112372 (Fry 1989). Most natural substances are depleted in ^{13}C relative to the V-PDB standard, and therefore have

negative ^{13}C ratios. The more positive a $\delta^{13}\text{C}$ value, the more ^{13}C it has relative to ^{12}C and to the standard and the 'heavier' it is (i.e., enriched in ^{13}C) (O'Leary 1988).

Natural Ranges of $\delta^{13}\text{C}$ Values

Carbon values from natural sources range from 0 to -110‰, compared to V-PDB (Boutton 1991a). Organic processes tend to discriminate against the heavier ^{13}C isotope, depleting organic matter in ^{13}C , resulting in its typically more negative $\delta^{13}\text{C}$ value. Carbon in inorganic materials tends to be enriched in ^{13}C relative to inorganic substances and is colloquially referred to as being 'heavier' (i.e., less negative) (Boutton 1991a).

2.3 OCEAN-ATMOSPHERE-SOIL-GROUNDWATER-GEOLOGY SYSTEMS

The carbon cycle can be further broken down into systems in order to understand how carbon moves through nature. When studying the groundwater dissolved inorganic carbon (DIC) derived from soil gas, the interaction between several of these systems must be examined.

Generally speaking, the oceans contain the largest amount of carbon, stored as sediments. The weathering of sedimentary carbon and the $\delta^{13}\text{C}$ values released may influence the atmosphere on very long time scales. The atmosphere holds a small percentage of the total carbon on the Earth, but serves as a major pathway of carbon in the global biogeochemical carbon cycle (Boutton 1991a). Atmospheric CO_2 diffuses into vegetation and is converted into an organic form during photosynthesis, dissolves in the

oceans and other bodies of water, and exchanges with gaseous CO₂ reservoirs, such as soil gas (Bolin 1979; Boutton 1991a). Carbon is found in the atmosphere mainly in the form of CO₂, although the minor trace gases such as CH₄ and CO contribute small amounts to the overall total atmospheric carbon reservoir (Freyer 1979a).

Atmospheric air, along with plant sources and volcanic fumes, can affect the $\delta^{13}\text{C}$ value and CO₂ concentrations in soils. This soil gas CO₂ will become dissolved in rainwater and affect the initial $\delta^{13}\text{C}_{\text{DIC}}$ value found in the groundwater. Furthermore, several chemical reactions may change the $\delta^{13}\text{C}$ values during transport within the aquifer, allowing geology to influence the $\delta^{13}\text{C}$ value, as well. Each system (ocean-atmosphere, atmosphere-soil, soil-groundwater, and groundwater-geology), can be separated into several processes.

Ocean-Atmosphere System

The atmosphere is a pathway between atmospheric inorganic C and terrestrial and oceanic organic carbon. Most of the carbon that dissolves into the ocean quickly dissociates into bicarbonate, the major form of carbon within the oceanic DIC (Boutton 1991a). Oceanic DIC ($\delta^{13}\text{C} \sim 0\text{‰}$) is the largest active pool of carbon on Earth and is in isotopic equilibrium with the atmosphere and oceanic carbonates (Boutton 1991a; Mook 2001). In bioremineralization, or respiration, photosynthesis by small marine organisms converts inorganic carbon into organic carbon, which then decays and either returns it to DIC form or as dissolved organic compounds (DOC). Carbonate-forming organisms also

remove calcium and bicarbonate ions from seawater, and then precipitate external shells (Bolin 1979). Most of the calcareous planktonic skeletons of these organisms and their waste settle down to the ocean floor and decay. The rest form deep sea sediments, such as limestone, which can store carbon for hundreds of thousands of years (Ruddiman 2001).

The bacterial decomposition of the organisms returns carbon to the deep sea, far away from organisms that may use them. The nutrients formed from this process are carried along the global ocean currents and released into the productive layers of the ocean as the water rises at coastal, equatorial, and high-latitude upwelling zones (Ruddiman 2001). Photosynthesis fractionates against ^{13}C , so surface waters rich in phytoplankton often have $\delta^{13}\text{C}$ values of 1 to 3‰, while decomposition of the ^{13}C -depleted organisms result in water with $\delta^{13}\text{C}$ values which are slightly heavier (0‰) (Boutton 1991a). Oceanic degassing and absorption of CO_2 controls the overall atmospheric $\delta^{13}\text{C}$ value, but over small time scales (less than hundreds of thousands of years), does not affect the atmospheric $\delta^{13}\text{C}$ value significantly (Ruddiman 2001).

Atmosphere-Soil and Atmosphere-Plant Systems

Atmospheric CO_2 affects soil CO_2 concentrations and $\delta^{13}\text{C}$ values in two ways: by directly infiltrating and exchanging with the soil gas, and through plants, which take up CO_2 for photosynthesis and then respire that CO_2 . First, general atmospheric $\delta^{13}\text{C}$

values and CO₂ concentrations will be discussed, then the effects that the two processes have on soil gas are addressed.

Atmospheric CO₂ Concentrations and $\delta^{13}C$ Values

Soils contain the largest active pool of carbon on land, with approximately 60 Gt C, or ten times the total amount of fossil fuel CO₂ delivered to the atmosphere per year (Rustad 2000). The concentration of CO₂ in the atmosphere currently averages 375 ppm (NOAA Climate Monitoring and Diagnostics Laboratory 2004). A strong seasonal signal is present in the atmospheric CO₂ record at all global measurement stations as a result of plants in the Northern Hemisphere taking up CO₂ during the summer growing period (Figure 2).

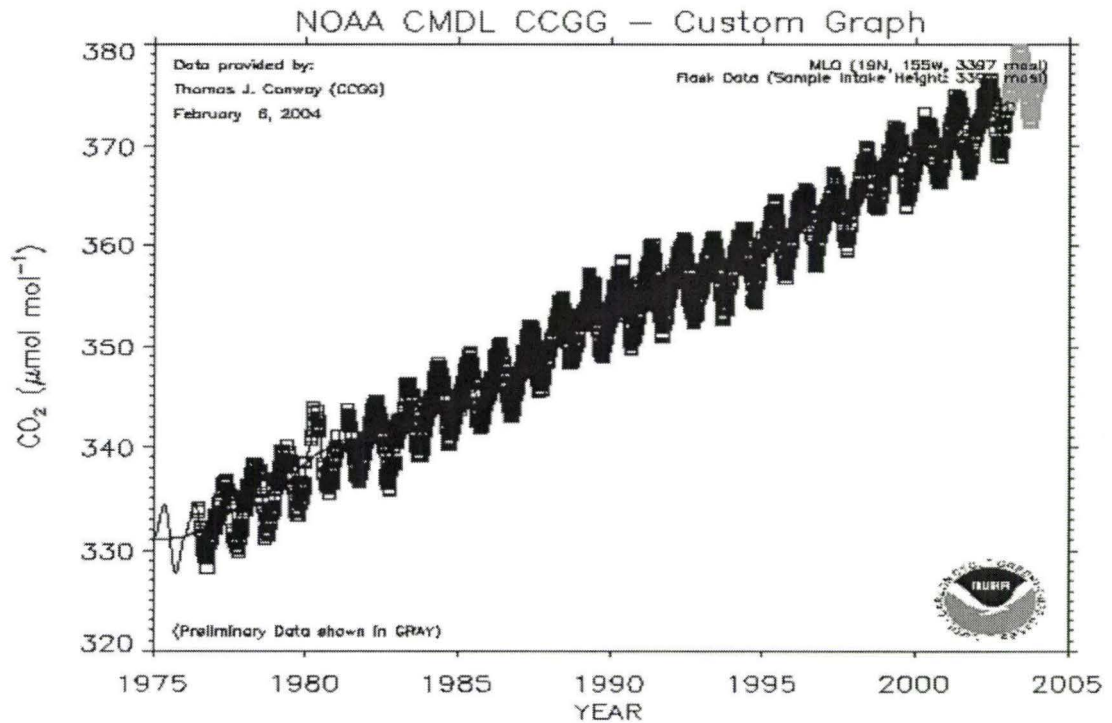


Figure 2. Atmospheric CO₂ with time. Seasonal trends are depicted (NOAA Climate Monitoring and Diagnostics Laboratory 2004).

CO₂ accumulates in the atmosphere during the winter as plants die, decay, and then emit the CO₂ stored in the plant over the growing season. Terrestrial net primary productivity is around 60 Gt of carbon per year, with approximately 850 Gt of carbon stored in plant biomass (Bramryd 1979).

The carbon in the atmosphere is comprised 98.9% of ^{12}C and 1.1% ^{13}C (O'Leary 1988). Since the ocean is a much larger C reservoir compared to the atmosphere, the overall atmospheric $\delta^{13}\text{C}$ value is chiefly controlled by ocean exchange over thousands of years. Smaller scale fluctuations (seasonal, diurnal) occur due to photosynthesis and the burning of fossil fuels. The current $\delta^{13}\text{C}$ value of atmospheric CO_2 is -8‰, and is becoming more negative as the combustion of isotopically light fossil fuel occurs ($\delta^{13}\text{C}_{\text{fossil fuel}} = -30\text{‰}$) (O'Leary 1988). The $\delta^{13}\text{C}$ value of the atmosphere fluctuates with the seasons, with the heaviest (i.e., less negative) levels after periods of high photosynthetic activity, during which vegetation preferentially absorbs the lighter isotope (Boutton 1991a; Boutton 1991b). Since the Northern Hemisphere contains larger land areas than the Southern, the $\delta^{13}\text{C}$ value will follow the Northern's seasons more closely. Therefore, the Northern Hemisphere's spring and summer growing seasons will cause the $\delta^{13}\text{C}$ value of the atmosphere to become heavier at those times. During the fall and winter, the $\delta^{13}\text{C}$ value will become lighter, due to the decay of vegetation and the return of the ^{12}C to the atmosphere (Figure 3) (Manahan 2000). In Hawai'i, seasonal changes are lessened by the proximity of the islands to the equator; the maximum $\delta^{13}\text{C}$ change is less than ~0.4‰ (NOAA Climate Monitoring and Diagnostics Laboratory 2004). The larger the atmospheric interaction with soil gas, the heavier the soil gas $\delta^{13}\text{C}$ values will become (leveling off at ~ -8‰).

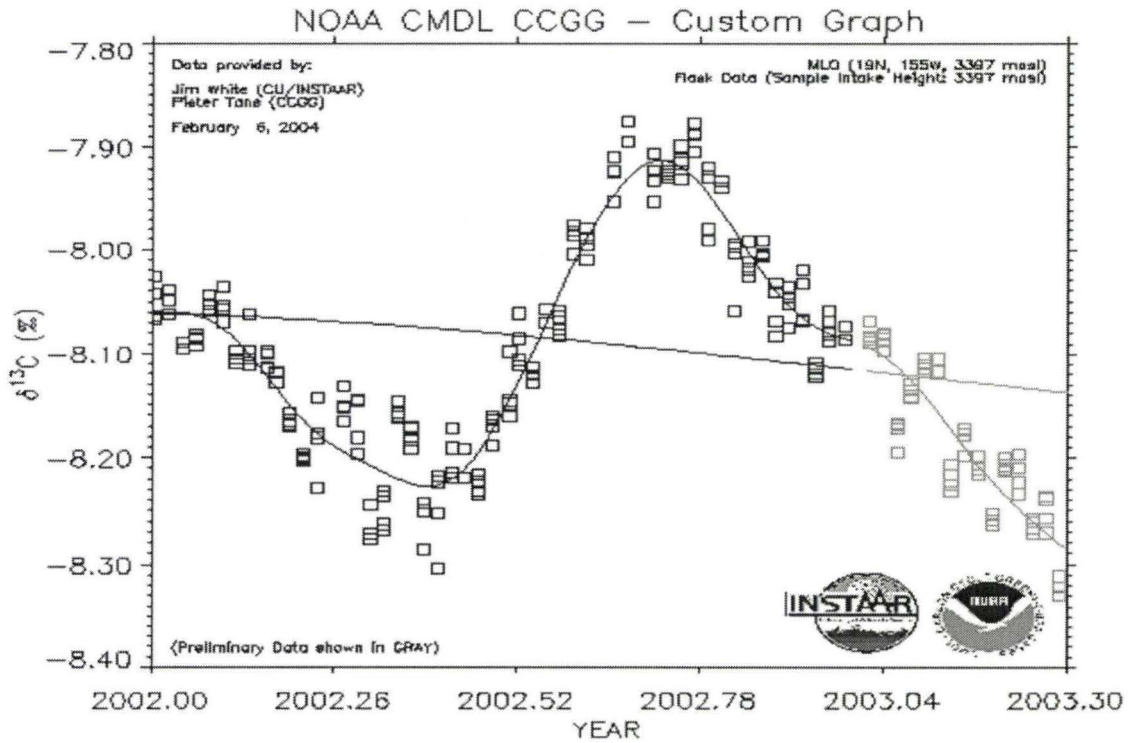


Figure 3. Atmospheric $\delta^{13}\text{C}$ Values from 2002 to 2004 at Mauna Loa Observatory. Gray data is preliminary. $\delta^{13}\text{C}$ values reflect seasonal trends. Range is from ~ -8.3 to $\sim -7.9\text{‰}$ (NOAA Climate Monitoring and Diagnostics Laboratory 2004).

Atmosphere-Soil System

Under certain conditions, atmospheric CO_2 can have a large impact on CO_2 concentrations in soil gas, due to exchange with and diffusion into and out of soils. According to one study, ambient CO_2 only affects the top 30 cm of soil (Boutton 1991a).

Models predict that atmospheric CO₂ is a significant contribution to soil air only at depths less than 10 cm, or when respiration rates are negligible (Dudziak 1996).

Exchange between soil gas CO₂ and atmospheric CO₂ can also strongly influence $\delta^{13}\text{C}$ values in soil gas. Again, this process is especially important near the soil surface. The depth to which this exchange influences the $\delta^{13}\text{C}$ value depends not only on the CO₂ diffusion rate and soil permeability, it is also strongly influenced by the root respiration rate occurring in the soil. The lower the rate, the deeper the influence of the atmosphere (Cerling 1991). Amundson (1998) found that CO₂ concentrations increased with depth and $\delta^{13}\text{C}$ values decrease from atmospheric values to the biological values enriched by diffusion with depth. The $\delta^{13}\text{C}$ values vary linearly with the reciprocal of CO₂ concentrations in soils where the $\delta^{13}\text{C}$ values of the CO₂ being produced are constant with depth (Amundson 1998). It follows that if a linear relationship can be established, the $\delta^{13}\text{C}$ value of the original source can be extrapolated.

Soil respiration

The production of CO₂ in soils cause diffusional gradients that result in a flux of soil gas CO₂ to the atmosphere (Andrews 1999). This soil-respired CO₂ is one of the largest fluxes to the atmosphere in the carbon cycle. While the term “soil CO₂” is given to the CO₂ occupying the space between grains of soil, “soil respired CO₂” is the flux of CO₂ exiting the soil due to diffusional gradients (Davidson 1995). Many more studies have been done on the flux of soil-

respired CO₂ than on the actual soil CO₂. These two reservoirs of carbon have different characteristics and should be treated as such.

As a result of the diffusional gradients and fluxes, the $\delta^{13}\text{C}$ values obtained from the soil gas CO₂ and soil respired CO₂ are different (Cerling 1991). The major mechanisms controlling these differences are diffusion and advection. The rate of escape of CO₂ strongly depends on soil characteristics such as porosity, grain size, and moisture levels (Dudziak 1996). In unsaturated soils, diffusion becomes the main control on gaseous movement under most conditions (Freijer 1996). Using diffusion equations, Cerling (1991) calculated an enrichment of $\delta^{13}\text{C}$ in soil gas CO₂ at least 4.4‰ compared to the CO₂ respired from the soil. (Boutton 1991a) found a similar enrichment of $\delta^{13}\text{C}$ in soil gas CO₂. According to his study, most soils have a CO₂ $\delta^{13}\text{C}$ value 5‰ heavier than would be expected based on photosynthetic plant type and SOM. Davidson (1995) argued that there is not a blanket fractionation value between soil gas and soil-respired CO₂; he found that the $\delta^{13}\text{C}$ value of the soil-respired CO₂ is actually what controls the magnitude of the difference between soil gas and soil-respired CO₂. When the difference between the atmospheric value and the soil-respired value is larger than 4.4‰, he calculated a minimum difference of 4.24‰ for a soil-respired $\delta^{13}\text{C}$ value of -36‰, and 4.36‰ for soil respired CO₂ with a $\delta^{13}\text{C}$ value of -9‰. For primarily C₄ dominated soil regimes, or other cases where the difference between the atmospheric $\delta^{13}\text{C}$ value and the soil-respired $\delta^{13}\text{C}$ value is less than 4.4‰, the minimum is just the difference between the two (Davidson 1995).

Diurnal trends in soil respiration are linked to temperature and microbial activity; many studies find that the highest fluxes occur in the afternoon, and the lowest just before dawn (Dudziak 1996). The maximum fluxes can reach levels greater than double the minimum. In the few studies that found that the maximum flux from the soil occurred at night, the anomalous high nocturnal fluxes were tentatively linked to changes in temperature, atmospheric air circulation, or humidity (Witkamp 1969; Edwards 1975).

Changes in CO₂ concentrations also occur throughout the seasons. (Hesterberg 1991) found the highest CO₂ levels during the spring growing season (when temperatures were high and vegetation was sprouting) and the lowest during the winter.

Canopy enrichment

In areas with dense canopy cover, atmospheric CO₂ concentrations and $\delta^{13}\text{C}$ values within the canopy may vary from reported atmospheric values, as ¹³C-depleted plant-respired CO₂ becomes trapped and reused by surrounding plants (Dudziak 1996; Buchmann 1997a; Buchmann 1997b). (Buchmann 1997a) found that $\delta^{13}\text{C}$ values near the soil in an Amazonian rainforest were more depleted in ¹³C than upper layers of the forest structure. These results are consistent with the findings of many similar studies (Sternberg 1989; Broadmeadow 1992; Francey 1995).

Canopy air can influence the isotopic signature of plant matter, which in turn is a factor in the $\delta^{13}\text{C}$ values of soil-respired CO₂ (Buchmann 1997b). A study in Utah found that the $\delta^{13}\text{C}$ value of soil organic matter (SOM) became enriched in ¹³C as leaf area

index (area of leaves overhead per unit ground area) increased (Buchmann 1997b). Even with the enrichment, the maximum difference in the $\delta^{13}\text{C}$ values of SOM with no leaf cover and SOM with leaf cover was 1‰.

Volcanic Sources

In areas with volcanic activity, CO_2 in soil may originate from the degassing of magma deep below the surface (Allard 1991). On Mt. Etna in Italy, concentrations up to 30% CO_2 by volume are found in the soil near the summit. CO_2 concentrations decrease with elevation down the volcano and with distance from rift zones and fractures (Allard 1991). In New Zealand, measurements of the CO_2 concentration over a geothermal field reached ~ 21 mole %. In contrast, CO_2 concentrations outside the volcanically active area were approximately 25% of that value (5.2 mole %). This smaller concentration was assumed to be composed entirely of CO_2 emitted from biologic sources (Finlayson 1992).

Gaseous emissions from magma stored under soils may diffuse upward to the atmosphere and change the $\delta^{13}\text{C}$ value of soil gas (Allard 1991). On Mt. Etna, values in the soil ranged from -3.3 to -0.3‰ at the summit, typical of $\delta^{13}\text{C}$ values of CO_2 near volcanic craters (Allard 1991). Further down-slope, $\delta^{13}\text{C}$ values became heavier either due to decreasing amounts of degassing at greater depths or the release of CO_2 due to heating of carbonates in the rocks. A study over a geothermal field in New Zealand reports $\delta^{13}\text{C}$ values of -4.2 and -8.1‰. Soil gas collected from nearby non-volcanic areas had $\delta^{13}\text{C}$ values near -25‰, which were attributed to plant and microbial respiration

(Finlayson 1992). Javoy (1986) reports $\delta^{13}\text{C}$ values of 0 to -10‰ in CO_2 from subduction zone volcanoes. $\delta^{13}\text{C}$ values of parent magma in Kilauea Volcano, Hawai'i, were -3.0 to -3.6‰, as found by Gerlach (1986). $\delta^{13}\text{C}$ values from fumaroles on Kilauea in later studies range from -2.8 to -3.4‰ (Gerlach 1990). In any case, CO_2 present in the soil from volcanic activity typically has an isotopic signature consistent with ^{13}C enriched magmatic CO_2 (greater than $\sim -10\text{‰}$) (Javoy 1986).

Atmosphere-Plant

In addition to atmospheric and volcanic sources, the respiration of plant roots and the microbial decay of detritus also may cause CO_2 to accumulate in the soil atmosphere (Andrews 1999). The relative contributions to soil CO_2 from each source depend on the degree of biological activity (which is highly correlated with soil moisture and temperature, and hence, climate and seasonality), soil type (particularly, the parameters of porosity, structure, grain size), and atmospheric pressure (Buyanovsky 1983). The biological sources of soil CO_2 are discussed, as well as how plant type may affect the resulting $\delta^{13}\text{C}$ values.

Microbial Respiration

Microbial respiration is one of the two main sources of soil gas CO_2 . Many kinds of microbes exist in soils—one square meter of soil may contain thousands of different types of microbes, as determined by DNA analysis (Freckman 1994). Numerous other

types of bacteria have not been identified but are postulated to exist—the importance of soil microbes and their diversity has only recently been recognized as a factor in future climate change. Differences in microbial communities across ecosystems, and how microbial communities evolve after a vegetation, temperature, or moisture change, are largely not well known, due to the lack of expertise, interest, and scientific methods developed in this area of science (Freckman 1994; Felske 2000; Hackl 2000; Henn 2000).

$\delta^{13}\text{C}$ values in carbon dioxide generated from the microbial decay of SOM have been found to be 1‰ lighter than expected, due to the slight discrimination toward ^{13}C by microbes (Dudziak 1996). Mary (1992) examined the progression of decomposition of three kinds of substrate in soil and found that the isotopic compositions of CO_2 from microbial respiration were 1.4, 0.6, and 1.7‰ more depleted in ^{13}C than the substrate composition. Mary (1992) theorized that the makeup of the microbial population changes depending on what stage of decomposition the substrate is in, and as a result, the CO_2 produced by the differing microbes in each stage will respire CO_2 with slightly different ^{13}C signatures.

Root Respiration

Root respiration is the main source of CO_2 in soil gas and has been studied in much greater detail. Growing season and environmental factors, such as temperature and moisture, may alter the CO_2 concentration and $\delta^{13}\text{C}$ value of root respired CO_2 , but the character of CO_2 derived from root respiration is chiefly determined by the plant type. In

fact, $\delta^{13}\text{C}$ values of root respired CO_2 are usually equal to or slightly more negative than the dominant photosynthetic mechanism of the surface vegetation (Dudziak 1996).

Vegetation

The dominant photosynthetic mechanism of vegetation in a region largely controls the $\delta^{13}\text{C}$ value in soil gas. Therefore, it is important to examine the different types of vegetation and the factors influencing their growth.

There are three types of vegetation, distinct in their photosynthetic mechanisms (Quade 1995). They each grow optimally under different conditions (temperature, moisture, atmospheric CO_2 levels, etc.) and the isotopic ranges of the two main types do not overlap (Quade 1995).

The assimilation of CO_2 from the atmosphere into a plant causes fractionation of that carbon. There are two steps in which fractionation occurs. The first is diffusion into the plant; this has been calculated to be 4.4‰, no matter what type the plant is. The second is during the transformation of the carbon into usable form by carboxylation. Since the method of carboxylation is different in the two plant types, the fractionation factor also varies by plant.

The most prevalent and primitive process is the C_3 mechanism, also called the Calvin cycle, and is used by trees and shrubs that thrive in areas with cool, rainy growing seasons (Quade 1995) and at high altitudes (Lee-Thorpe 1990). C_3 plants are the most common worldwide, and make up a majority of forest and temperate zone vegetation (Boutton 1991a). The $\delta^{13}\text{C}$ values for C_3 plants range from -23 to -35‰, with an average

around -26 or -27‰ (Cerling 1993; Quade 1995). The range of the value is due to the isotopic variation in plant species and the effects of different amounts of light and moisture (Cerling 1993; Quade 1995).

In C_3 plants, CO_2 enters the leaf through the stomata and diffuses into the mesophyll cells where ribulose biphosphate carbonxylase/oxygenase (Rubisco) catalyzes the carboxylation of ribulose biphosphate (RuBP) to form a 6-carbon compound. Light is used to transfer electrons to nicotinamide adenine dinucleotide phosphate (NADP) and to generate adenosine triphosphate (ATP). These compounds provide energy to separate the 6 carbon molecule into two 3-phosphoglycerate molecules (PGA; a three carbon molecule) by hydrolysis (Ehleringer 1993).

In the reduction sequence, a phosphate group is added to PGA using ATP, then 1,3 diphosphoglycerate takes a proton and 2 electrons from NADPH to yield glyceraldehyde phosphate, or PGAL. Some of carbon end-product of photosynthesis, PGAL (along with ATP) is then used to reform RuBP, while the one leftover molecule is used within the plant to form carbohydrates such as sugars and feed the plant (Ehleringer 1993).

The Calvin cycle is used in most plants today. However, in spite of its prevalence, it does have its downfalls. Plants use stomata to regulate their intake of CO_2 and output of moisture. In hot, dry environments, stomata will close to save the plant from losing all their moisture and dying. Closing their stomata cuts off the plant from further CO_2 intake, allowing the O_2 concentration within the plant to increase as CO_2

becomes used up in photosynthesis. Rubisco (the enzyme used to catalyze carboxylation) has an affinity for both CO_2 and O_2 ; when the oxygenase reaction occurs, it wastes energy and causes the plant to photorespire that CO_2 . As O_2 concentrations increase, the CO_2 : O_2 ratio lowers, and Rubisco chooses to react with O_2 more and more. The plant, in effect, becomes less and less efficient. At 25 °C, the Rubisco combines with O_2 one out of 5 times—it is 20% inefficient. At higher temperatures, Rubisco's affinity for O_2 compared to CO_2 is greater, so C_3 plants become more inefficient at higher temperatures (Ehleringer 1993).

In response to this inefficiency, the Hatch-Slack (C_4) pathway evolved sometime in the Miocene Epoch (23 to 5 My), possibly due to the low CO_2 concentrations typical of that time (Quade 1995). C_4 plants evolved a way to increase CO_2 concentrations near Rubisco. Instead of having one mesophyll cell in which the carboxylation reactions take place, C_4 plants have both “mesophyll” and “bundle sheath cells.” Reactions and chemicals specific to C_4 plants are found in the outer mesophyll cell, while C_3 reactions (“Calvin cycle reactions”) are located in the bundle sheath cells. The mesophyll cell is where the CO_2 enters the plant, is converted to HCO_3^- , and reacts with phosphoenyl pyruvate (PEP) to form oxaloacetate. This compound is then transformed to malate (a 4-carbon acid), which is then carried into the bundle sheath cell, where normal Calvin cycle photosynthesis occurs after the malate is decarboxylated into pyruvate and CO_2 . The pyruvate is then used to create PEP in the mesophyll cell (O'Leary 1988). Normal C_3 reactions take place in the bundle sheath cell after the decarboxylation occurs, but the

differences lie in the O₂ content—virtually no photorespiration occurs in C₄ plants. The extra step concentrates CO₂ within the plant, and allows the plant to open or close their stomata without decreasing efficiency. The CO₂ is sequestered in the bundle sheath cell until it is needed in the plant. This allows C₄ plants to outperform C₃ plants in times of low pCO₂ and in dry and hot conditions (the opening of stomata to acquire CO₂ in these conditions also makes the plant lose water). The downfall, however, lies in the extra energy it takes to take the CO₂ in the 4-C acid to the Rubisco. In low to moderate temperatures, this extra energy is greater than the inefficiencies associated with photorespiration in C₃ plants (Collatz 1998).

Plants using the C₄ pathway are found in regions with warm growing seasons and consist of grasses and sedges (Cerling 1993). These plants are prevalent in tropical grasslands and are found in low latitude and altitude regions (Boutton 1991a). C₄ isotopic values are usually -10 to -14‰, with an average of -13‰ (Cerling 1993).

The difference in δ¹³C values in C₃ and C₄ plants occurs due to the various reactions CO₂ goes through in each type of plant. An initial, diffusive fractionation of 4.4‰ occurs in both plants as CO₂ is assimilated into the plant (O'Leary 1981). In C₃ plants, a fractionation of ~30‰ occurs during the carboxylation of RuBP due to the high aversion to ¹³C by the catalyst Rubisco (Hayes 2001). The fractionation that occurs when atmospheric CO₂ is converted to bicarbonate favors ¹³C and is -9‰ (Ehleringer 1993). The enzyme (PEP carboxylase) in C₄ plants that acts as a catalyst discriminates against ¹³C to a much lesser degree (2‰), giving C₄ plants heavier δ¹³C values (Hayes 2001).

The total fractionation from gaseous CO₂ to PEP carboxylation is around -5.7‰ in C₄ plants (O'Leary 1981). While C₄ plants still use Rubisco in their bundle sheath cells to carboxylate the sequestered CO₂, the amount of ¹³C in the CO₂ presented to the Rubisco is larger, also decreasing the amount of fractionation occurring. The large amount of CO₂ that C₄ plants are able to store (10 to 15 times the quantity found in the mesophyll cell) due to the extra step allows the plant to be more efficient in its Rubisco use. This process uses more ATP (energy) than C₃ plants, and the large gradient of CO₂ within the leaf compared to the atmosphere causes leakage across the plant tissues. This leakage is thought to be the cause of additional fractionation in C₄ plants, though still not to the extent that occurs in C₃ plants (O'Leary 1981).

The third photosynthetic pathway in vegetation, Crassulacean Acid Metabolism (CAM), combines characteristics of both the C₃ and C₄ mechanisms. During the night, the plant engages in C₄-type photosynthesis; by day, the plant processes CO₂ using the C₃ mechanism. Consequently, CAM plants' isotopic signatures are a mixture of those from C₃ and C₄; they range from -10 to -20‰ (O'Leary 1988). CAM plants are abundant in deserts and other arid areas, but they are found in very few areas in Hawai'i.

The massive volcanoes on the Island of Hawai'i divert the flow of tradewinds and create a rain shadow, resulting in a desert-like environment downwind of the volcano. Summit regions of these large volcanoes are also above cloud altitudes and receive little to no moisture (Mueller-Dombois 1998). This area and its vegetation is assumed to have little, if any, affect on the δ¹³C value found in the HSDP groundwater since this desert is

located far outside of the presumed recharge area for the windward Mauna Kea aquifers: it receives small quantities of rain that could contribute to groundwater bodies and it is very sparsely vegetated.

Environmental conditions and metabolic pathways

Temperature and CO₂ concentrations are the major controls on the dominant photosynthetic mechanism for a region or during a geologic time (Kuypers 1999). The metabolic pathways are constrained by CO₂ levels and climate regimes, a reflection of the conditions under which each pathway evolved (Cerling 1993). During times of low CO₂ concentrations, the C₃ pathway gave way to the C₄ and CAM mechanisms in order to adjust to the changing climatic conditions (Ehleringer 1997). Lower pCO₂ in glacial times has indeed been linked to the evolution and expansion of C₄ grasses (Cerling 1993; Cole 1994; Kuypers 1999). In the C₄ mechanism, plants pump and concentrate CO₂ within their cells, overcoming the low CO₂ pressure in the atmosphere (Cole 1994; Kuypers 1999). These plants have an advantage over C₃ plants during times of low pCO₂ and high temperatures (Kuypers 1999). It is estimated that below 400-500 p.p.m.v. of CO₂, C₄ plants are more efficient than C₃ (Cerling 1993; Kuypers 1999). At higher levels of CO₂, the C₄ mechanism takes more energy to maintain than it produces (Kuypers 1999). C₄ plants also outperform their counterparts in conditions of water stress and high temperatures (Cerling 1993), which leads to the conclusion that they are the more water-efficient of the two (O'Leary 1988). C₄ plants are dominant where an average daily

temperature above 25°C is maintained during the growing season, and the minimum temperature is 8°C or higher (Lee-Thorpe 1990). C₃ grasses are more common where the rainy season falls in the winter and at high elevations (Lee-Thorpe 1990).

Temperature and rainfall conditions determine the crossover elevation at which the dominance of C₄ grasses of the vegetation gives way to C₃ grasses. Studies have found that the most reliable determinant in crossover elevation is the mean minimum and maximum temperature of the warmest month (Cabido 1997). In more temperate climates, the crossover elevation is at the altitude where average minimum and maximum July temperatures are 15 and 29 °C, respectively. Tropical areas, however, show a different trend. A study of vegetation in Hawai'i Volcanoes National Park found a crossover elevation of around 1400 m, which corresponds to minimum and maximum temperatures of 9 and 21 °C (Rundel 1980). C₄ dominance with similarly cool temperatures has been duplicated and supported in numerous other studies examining grass crossover dynamics in other tropical areas, such as Costa Rica, Kenya, Argentina, and Australia (Chazdon 1978; Tieszen 1979; Hattersley 1983; Cabido 1997). The year-round virtually constant temperatures found in tropical areas is thought to account for this difference in crossover dominance temperature between latitudes (Rundel 1980).

In Hawai'i, approximately two-thirds of grasses are C₄ (Rundel 1980). On Mauna Kea, C₄ grasses start to reach their limit (but do not become absent) around 1850 m; beyond this elevation, C₃ grasses become increasingly more prevalent.

Root vs. Microbial Respiration

While multitudes of studies have quantified soil fluxes, only tens of papers have addressed the relative contributions of the sources of CO₂ within the soil, particularly root and microbial respiration. These processes are important to the understanding of the carbon cycle. SOM carbon storage rates and live root contributions to CO₂ are required to balance the carbon budget (Raich 1992). Current models suggest that even small changes in decomposition rates or production rates of plant matter can have profound impacts on the carbon balance in the biosphere that could significantly impact global climate (Raich 1992; Hanson 2000). The difficulty in quantifying root versus microbially respired CO₂ without significantly altering the soil environment has limited the number of studies on this subject (Ekblad 2000). Root respired CO₂ and microbially produced CO₂ are particularly hard to separate due to their similar substrate compositions. Plant type (C₃, C₄, or CAM) is the controlling influence on root respired CO₂ δ¹³C values. Once the plant dies and becomes a part of SOM, microbes decomposing that plant material will respire CO₂ with δ¹³C values matching the δ¹³C values of the substrate. In areas where vegetation type has not changed recently, microbes and roots will respire CO₂ with similar δ¹³C values (Schubler 2000).

The several attempts that *have* been made to separate CO₂ sources in the soil produced a wide range of results. (Raich 1992) states that a majority of studies find that live root respiration constitutes 30 to 70% of the CO₂ soil flux, while a compilation of many studies by (Hanson 2000) reports that root respiration contributes 10 to 90% of the

soil flux. The major causes for the wide range of results are season, vegetation type, and the numerous methods that have been developed to determine root versus microbial respiration (Hanson 2000).

CO₂ Concentrations and $\delta^{13}C$ Values in Soil Gas

The combinations of the sources described earlier (root respiration, microbial respiration, volcanic sources, and the atmosphere) result in soil gases with partial pressures of CO₂ far above atmospheric levels (~0.037%) (Wood 1984). In fact, soil CO₂ levels 1000 times higher than the ambient atmosphere have been found (Freyer 1979b).

Soil gas CO₂ concentrations vary throughout the soil column. Near the surface, CO₂ levels are generally low and increase with depth. Dudziak (1996) postulates that this phenomenon occurs due to the greater interaction of ambient air with the upper soil layers as compared to deeper portions of the soil profile. One study carried out in Switzerland found that the measurements of CO₂ concentration at 30 cm in the soil were 1 to 3.5% CO₂, while levels at 80 cm were 2.5 to 5.5% CO₂ (Hesterberg 1991).

As a consequence of high CO₂ levels within soils, concentration gradients develop between the soil horizon up to the atmosphere or down to groundwater (Wood 1984). The flux to the atmosphere is what is earlier described as “soil respiration.”

$\delta^{13}\text{C}$ values of soil gas CO_2

Low respiration and decay rates or entry of ^{13}C -rich atmospheric CO_2 may cause enhancement of the $\delta^{13}\text{C}$ value. In most cases, CO_2 concentration increases inversely with ^{13}C content with depth in the soil. Due to the various sources of CO_2 in soil, each differing in their $\delta^{13}\text{C}$ signature, $\delta^{13}\text{C}$ values change according to CO_2 concentration (Dudziak 1996). Dudziak (1996) explains that this is due to the soil flux of CO_2 to the atmosphere and atmospheric mixing with the upper layers of the soil column. $^{12}\text{CO}_2$ exits the soil faster than $^{13}\text{CO}_2$ because of mass differences affecting their diffusion coefficients. ^{12}C preferentially diffuses into the atmosphere before ^{13}C , enriching the soil environment in ^{13}C when soil respiration is low. This produces a 4.4‰ enrichment of $\delta^{13}\text{C}$ in soil gas CO_2 compared to the original $\delta^{13}\text{C}$ value of the respired CO_2 . In this process, the soil characteristics (moisture, grain size, porosity, permeability, etc.) control the rate of escape of CO_2 , and therefore, the amount of enrichment (Dorr 1980). Models predict the decrease in the amount of ^{13}C with increasing depth and respiration rate; as more ^{13}C -deficient (i.e. plant) CO_2 respire into the soil atmosphere, ^{12}C ‘floods’ the remaining, diffusion-enriched ^{13}C in the soil gas. This process causes the $\delta^{13}\text{C}$ value to become lighter, as long as there is a constant respiration rate and a decline in respiration with depth (Dudziak 1996). The greater the root and microbial respiration, the more ^{12}C is introduced to the soil atmosphere, so disregarding plant type differences, the lighter the $\delta^{13}\text{C}$ value, the greater the CO_2 concentration.

In addition, atmospheric pressure fluctuations may act to change the depth of atmospheric infiltration in the soil. If pressure increases, atmospheric air will penetrate farther into the soil profile, increasing the amount of ^{13}C -rich atmospheric CO_2 , but decreasing the CO_2 content due to the low concentrations in atmospheric air (Dudziak 1996).

Diurnal variations in $\delta^{13}\text{C}$ values

While diurnal variations in soil respiration fluxes have been extensively measured in the past six decades, none of these studies focused on $\delta^{13}\text{C}$ values of CO_2 *within* the soil (Dudziak 1996). In most studies of soil-respired CO_2 , the lightest $\delta^{13}\text{C}$ values are found during daylight hours, when root respiration is at its peak and CO_2 concentrations are at their highest (Huck 1962; Dudziak 1996). Values are usually a few per mille heavier during the night hours (Dudziak 1996). Most studies cite temperature differences as the cause for the lower CO_2 soil flux at night, but other studies show that photosynthetic cycles, independent of temperature, are also responsible for triggering root respiration (Kuzyakov 2001).

Many previous investigations have also studied the diurnal changes in atmospheric $\delta^{13}\text{C}$. These studies found a 2 to 6% change in the $\delta^{13}\text{C}$ value throughout the day. They concluded that ^{13}C was most abundant in the atmosphere during the afternoon and decreased in the hours before dawn, probably due to plants taking up ^{12}C during the day, increasing the relative amounts of ^{13}C (Dudziak 1996).

Dudziak (1996) performed a study on cultivated and forest sites in southeastern Poland to quantify diurnal variations in the $\delta^{13}\text{C}$ values during the growing season. They also found definite cycles of concentration and $\delta^{13}\text{C}$ in soil gas CO_2 . In warm temperatures, virtually no changes in $\delta^{13}\text{C}$ occurred, perhaps due to consistent microbial action. In the forest region, the smallest CO_2 concentration and heaviest $\delta^{13}\text{C}$ values occurred at sunrise, while these conditions occurred during the afternoon in the agricultural field. $\delta^{13}\text{C}$ values correlated with carbon dioxide concentration at all sites. Their study illustrates the importance of sampling at consistent times of the day when collecting soil gas CO_2 .

Seasonal variations in $\delta^{13}\text{C}$ values

$\delta^{13}\text{C}$ values produced in the soil will also change with season. In one study of a Polish forest by Dudziak (1996), May values ranged from -16 to -20‰, while August values were lighter (-18 to -22‰). Hesterberg (1991) found the lightest $\delta^{13}\text{C}$ values during the growing season due to the increased root respiration and temperature.

The Effect of Temperature and Moisture

Overall, the production rates of each of the main CO_2 sources in soil are determined by a multitude of factors that vary both diurnally and seasonally (Hesterberg 1991; Dudziak 1996). Many studies have revealed that soil gas CO_2 levels are correlated most closely with soil temperature, and to a lesser degree, moisture (Yamaguchi 1967;

Buyanovsky 1983). A study by Buyanovsky (1983) found that as temperature rose and fell through the seasons, the CO₂ concentration in the soil followed suit. Once the threshold temperature was achieved, soil moisture played a role in the CO₂ level; as moisture levels increased, CO₂ concentrations rose with them. This trend seems to be correlated with biological activity—once temperatures reach a level suitable for microbial activity, decay is stimulated and CO₂ starts to accumulate in the soil. After temperatures became higher than the minimum temperature threshold, increased moisture allows further decay and accumulation of CO₂ to occur (Buyanovsky 1983). In their experiment, the lower limit of temperature was approximately 10 °C; above this temperature, soil moisture could have an effect on soil gas CO₂ levels. Below this temperature, however, soil moisture was not correlated with CO₂ level. Soil moisture is an important influence on soil CO₂ concentrations, and therefore, δ¹³C values. When soil is wet, it decreases the exchange of atmospheric air with the soil air, while also stimulating microbial activity, resulting in increasing CO₂ concentrations (Dudziak 1996). One study found significant variations in the CO₂ concentrations and δ¹³C values in dry soil (0.2% to 0.4%; -16 to -21‰) as compared to wet soil (0.2% to 0.55%; -17 to -22‰) (Dudziak 1996). Maxima of concentrations correspond to the most depleted values and occur just before dawn in a deciduous forest.

Another study, however, found that intense rainfall events may decrease productivity. In the case where 60 mm of rainfall fell in a 48 hour period, Hesterberg

(1991) discovered that the CO₂ concentrations decreased rapidly. They attributed the drop in CO₂ production to the decrease in microbial activity.

Soil-Groundwater System

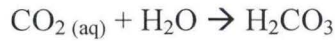
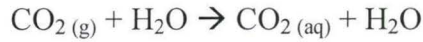
Diffusion gradients play an important role in the movement of soil CO₂ to the atmosphere or nearby soil horizons (Buyanovsky 1983). These concentration gradients allow soil gas CO₂ to diffuse into groundwater, thereby affecting the carbonate content of the water (Buyanovsky 1983). Another way CO₂ enters the aquifer system is through rainwater. Soil gas CO₂ dissolves into rainwater percolating through soil horizons to aquifers (Hendry 1993). Carbon dioxide is moderately soluble, and it dissolves readily into rainwater or groundwater to form carbonic acid. It then loses protons to form bicarbonate and carbonate, as in the reaction below:



(Yamaguchi 1967; Mook 2001).

The amount of CO₂ that dissolves into water is a function of temperature and the partial pressure of CO₂. The lower the temperature and higher the pressure, the greater the solubility of CO₂. Higher temperatures give the gas energy to leave the liquid; higher pressures allow the gas molecules to crowd together, making space for more gas molecules in the liquid. Henry's Law states that at low pressures, the amount of gas that

dissolves into a solute is equal to the pressure times a constant (K_H), where K_H is dependent on temperature (Manahan 2000). H_2CO_3 forms in the following manner:



The concentration of CO_2 in the water is set equal to H_2CO_3 . Freshwater can be considered an ideal solution, effectively allowing the thermodynamic equilibrium constant (including the activity coefficient γ) to equal the apparent constant, or

$$(2) \quad K_H = \frac{H_2CO_3}{PCO_2}$$

where P is in atmospheres and K is moles per liter, and the H_2CO_3 concentration is in moles per kilogram of water (Mook 2001). H_2CO_3 then dissociates to H^+ and HCO_3^- .

The pH and salinity of the water determines the dominant species of carbon in the water (Figure 4). At pH's of ~ 6.4 or less, the major species is H_2CO_3 . Above pH's of 10.5 or more, carbonate dominates. At neutral pH's, the amount of carbonate is insignificant and the main species is bicarbonate (Figure 4) (Yamaguchi 1967).

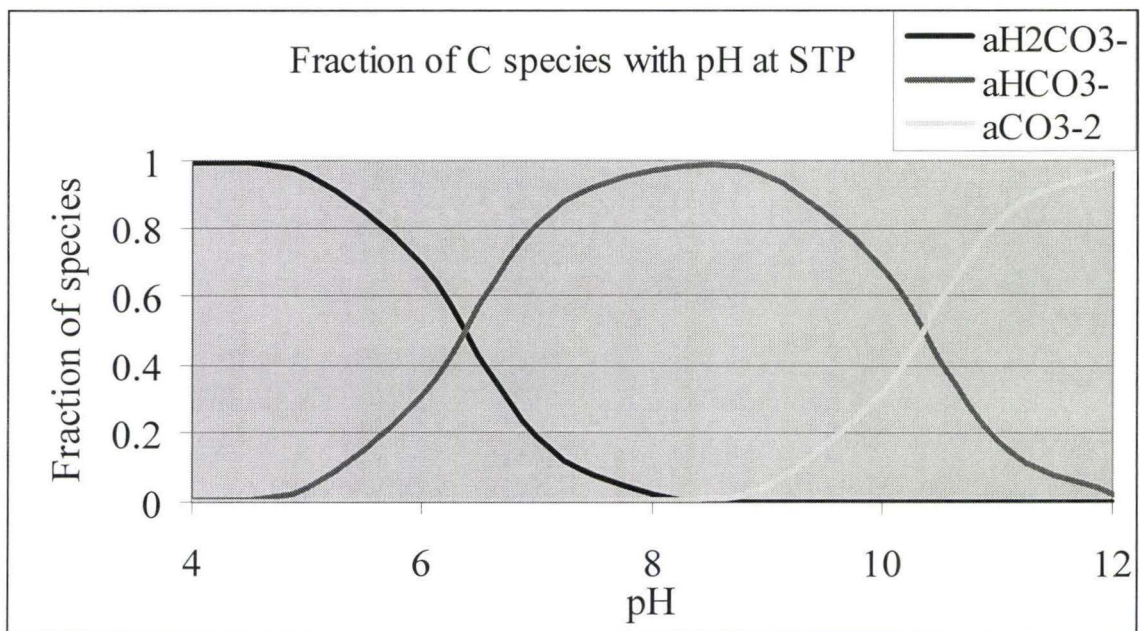


Figure 4. Distribution of carbon species as fraction of total carbon dissolved in water with pH at 25 °C. Low pH's are dominated by carbonic acid, neutral pH's by bicarbonate, and basic solutions by carbonate.

Groundwater $\delta^{13}\text{C}$ values in dissolved inorganic carbon (DIC) have a wide range, but are usually between -10 and -25‰ (Boutton 1991a). $\delta^{13}\text{C}$ values of DIC in the entering groundwater depend on the composition of the atmospheric and soil gas CO_2 that has dissolved into the rainwater recharging the aquifer (Figure 5).

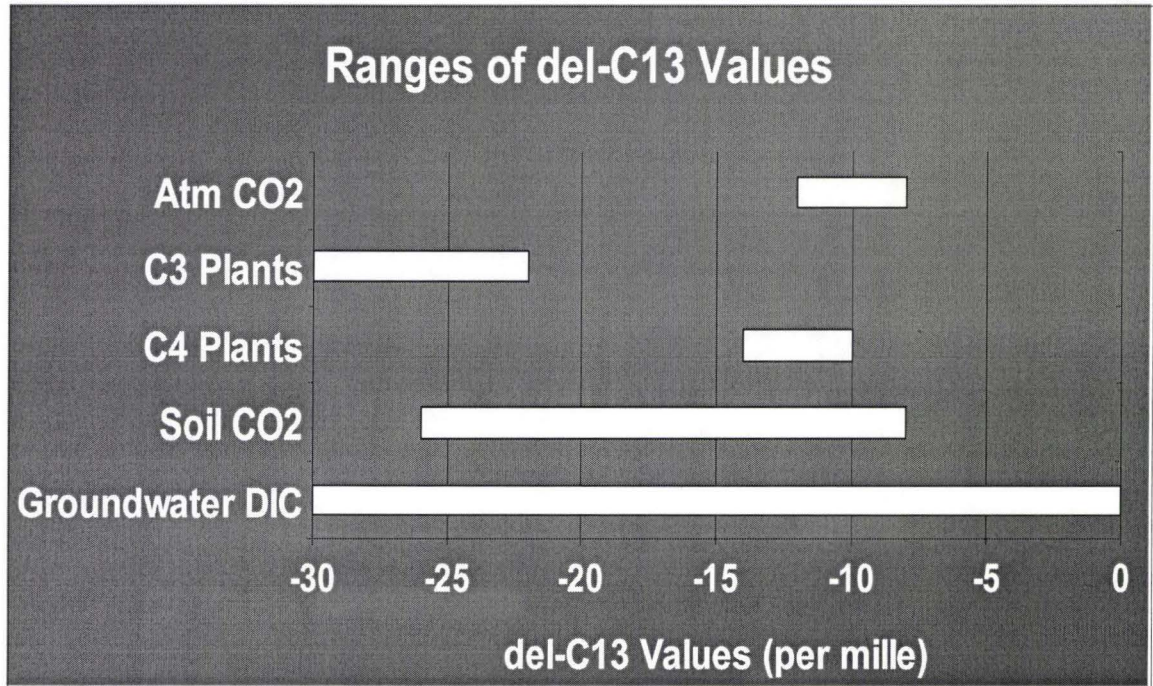


Figure 5. Ranges of ^{13}C values of various substances (after Boutton 1991a; Dudziak 1996).

^{13}C values in DIC are usually heavier than soil gas values, due to fractionation of carbon during the dissolution of CO_2 into water and the deprotonation of H_2CO_3 into bicarbonate and carbonate (Paull 2000). Bicarbonate in groundwater is approximately 6‰ heavier than CO_2 in soil gas (Voss 1994).

Groundwater-Geology System

Acid-base (calcite dissolution and deposition) and reduction-oxidation (redox) reactions are the major ways that the $\delta^{13}\text{C}$ value of DIC may be changed (Clark 1997).

Redox reactions in groundwater consist of the transfer of electrons from a reductant to an oxidant (Manahan 2000). Microbes obtain energy through mediating

redox reactions. They wish to gain as much energy as possible from processing materials, so they will attack oxidants preferentially, in order of oxidation potential. From greatest energy gain to lowest, the most common oxidants in groundwater are O_2 , NO_3^- , MnO_2 , $Fe(OH)_3$, SO_4^{2-} , and CO_2 (Manahan 2000). Most aquifers are zoned in this manner, with dissolved oxygen as the oxidant near the recharge source and with oxidants further down the chain used deeper into the aquifer, as each source becomes exhausted (Puckett 2002).

Initially, aerobic microbes will oxidize the available DOC in the water, until the DOC or oxygen supply is depleted. If the reactions are oxygen-limited, anaerobic microbes will start to use other oxidants to process the remaining organic matter once all oxygen is exhausted. As the supply of each oxidant decreases in turn, the next available oxidant in the chain will be utilized. Denitrification (the reduction of nitrate to nitrogen gas) is the first of these redox reactions to occur when conditions become anoxic enough (Puckett 2002). The reduction of manganese and ferrous oxides will occur next, if available, then sulfate reduction, and finally, methanogenesis. Methanogenesis is energetically inefficient, and only occurs in anoxic waters very low in nitrate and sulfate (Manahan 2000).

Each of these processes utilizes an electron donor to convert the carbon in organic matter into carbon dioxide. The $\delta^{13}C$ value in DIC and DOC is subsequently changed by each of these reactions. Since it is easier to break lower-energy bonds in ^{12}C , microbes preferentially fractionate against ^{13}C . Redox reactions also change the $\delta^{13}C$ value by

changing the alkalinity of the water. Alkalinity rises with each advancement down the oxidant chain, increasing the $\delta^{13}\text{C}$ value of DIC. The waters become supersaturated with respect to calcite, eventually leading to calcite precipitation, removing DIC and Ca from the waters and further fractionating the carbon in the DIC (McIntosh 2004). The precipitation of calcite from DIC decreases the $\delta^{13}\text{C}$ value by around 2‰, while calcite dissolution ($\delta^{13}\text{C}$ value of 0‰) will increase the $\delta^{13}\text{C}$ value (as long as the initial $\delta^{13}\text{C}$ value is less than 0‰, as in most cases) by an amount proportionate to its dissolution (Kendall 1998).

If these processes are occurring in the groundwater, one expects to see the products of reduction (methane, sulfide, nitrogen gas, calcite), as well as an increase in the $\delta^{13}\text{C}$ value. Usually, contaminated, organic-rich groundwaters are the only groundwaters which contain enough organic matter to both exhaust the oxygen supply and provide enough oxidants for these reactions to occur (Chapelle 2000). In uncontaminated groundwaters, very little organic carbon or other oxidants are present. Consequently, waters do not become anoxic enough for further reduction to take place, and therefore do not change the $\delta^{13}\text{C}$ value significantly (Pettersson 1994; Frimmel 1998).

CHAPTER 3

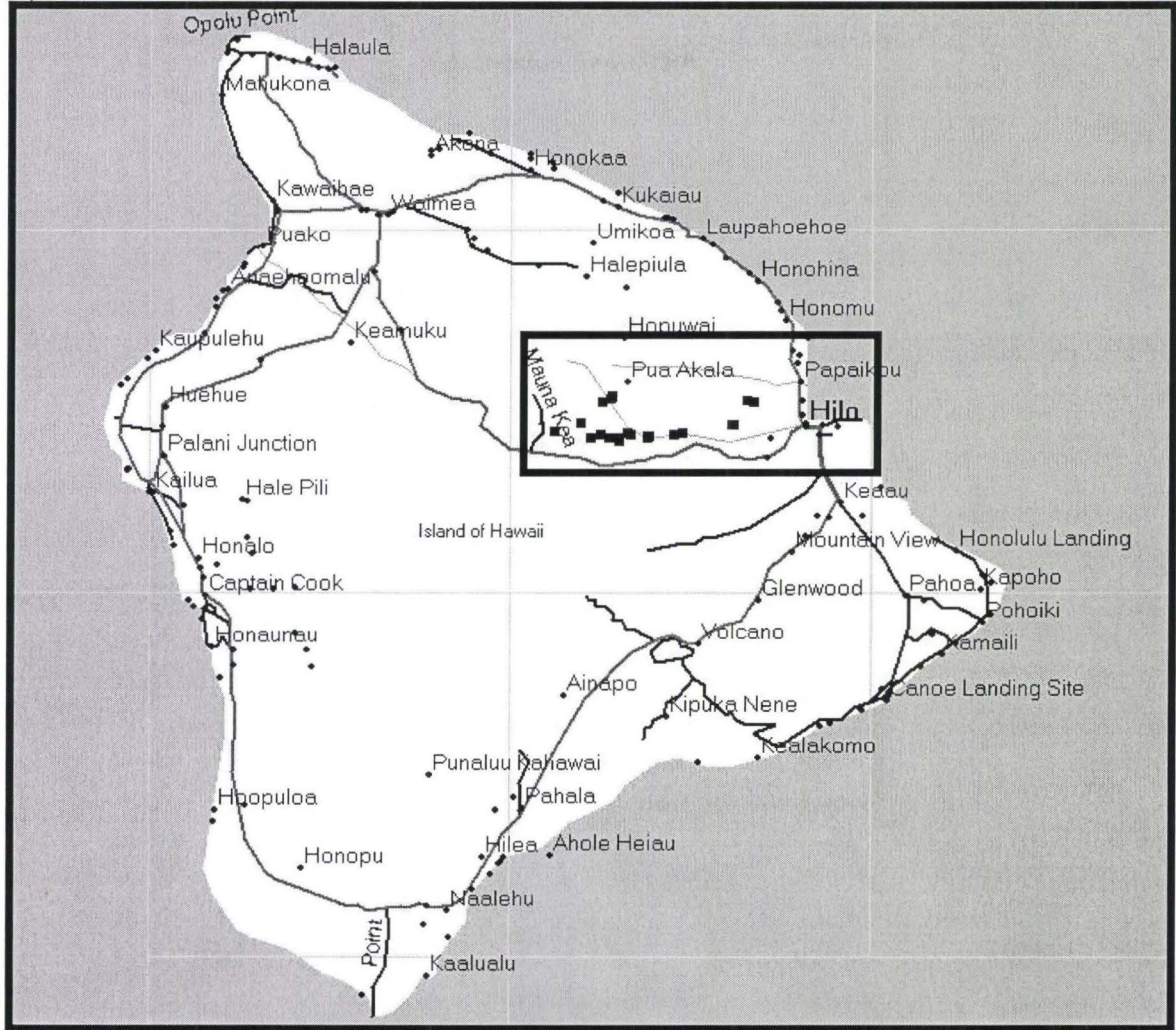
SITE DESCRIPTION, METHODS, AND MATERIALS

CO₂ concentrations within soils are at much higher levels than in atmospheric air, which makes the collection and analysis of CO₂ simpler than many other gases. Virtually no enhancement of CO₂ concentrations is necessary to introduce gaseous CO₂ into a machine (GC-MS) and analyses are very straightforward.

3.1 GENERAL SITE DESCRIPTION

The transect was located on the southeastern flank of Mauna Kea, a dormant volcano located in the eastern portion of the Island of Hawai'i. A transect spanning 500 m to 2100 m in elevation was chosen for its proximity to the postulated recharge zone identified in the HSDP boreholes (Figure 6).

a)



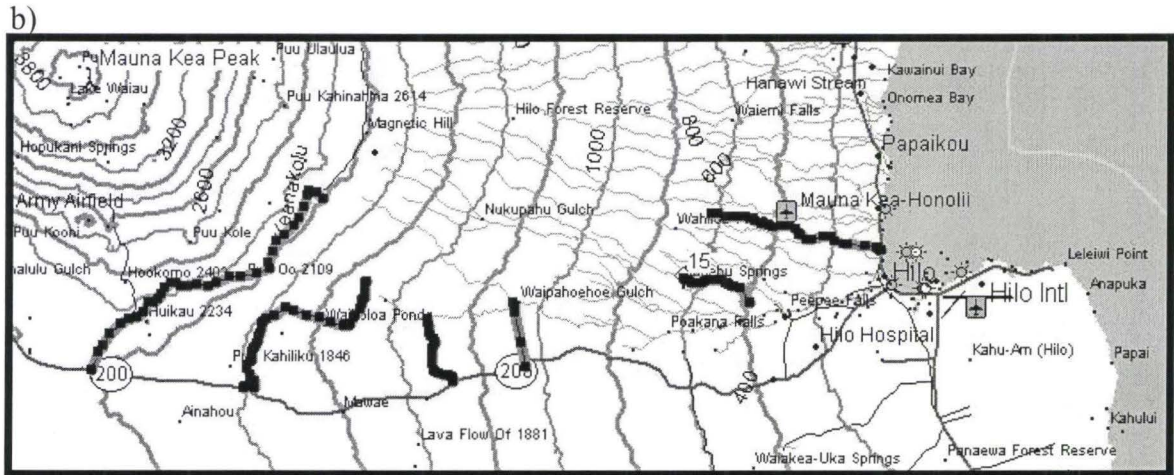


Figure 6. Maps of transect areas. a) The Island of Hawai‘i with the transect area boxed. b) Boxed area--purple tracks represent the six areas samples were taken. Areas are numbered from lowest elevation to highest. Contours are 200 m apart; north is to the top of the map.

Six areas were selected for soil gas sampling based on their locations on Mauna Kea soil, their relative accessibilities, and vegetation. From lapse rate calculations ($-6.5\text{ }^{\circ}\text{C}/1000\text{ m}$ below 1200 m; $-4.0\text{ }^{\circ}\text{C}/1000\text{ m}$ above 1200 m) and recorded average annual temperatures at various elevations, it is possible to extrapolate average annual temperatures in the areas studied in this investigation (Table 1) (Sanderson 1993).

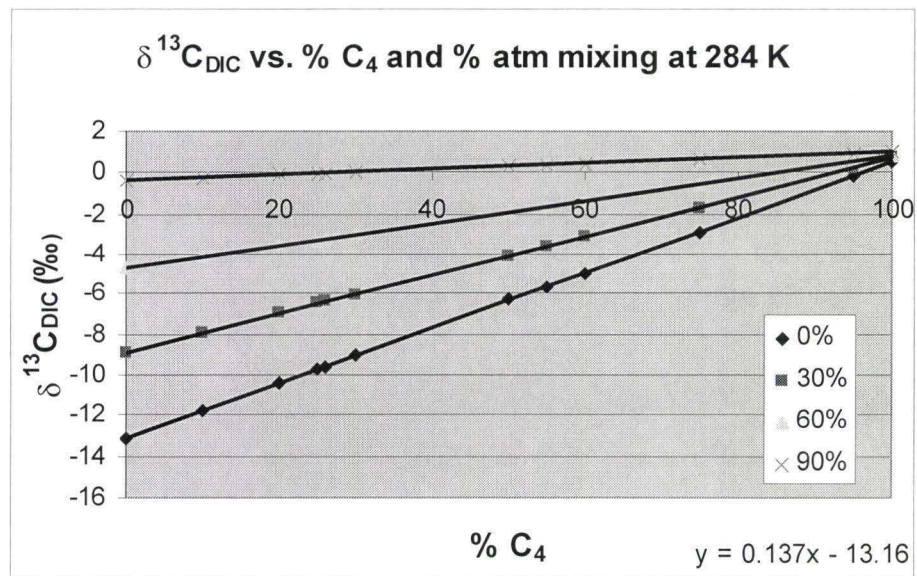
Table 1. Average annual temperature at elevations used in this study (*taken from Sanderson, 1993; all other temperatures were calculated using this temperature and the appropriate lapse rate).

Area	Elevation (m)	Mean Annual Temperature (MAT) (°C)
5 and 6	700	19.65
4	1000	17.7
3	1300	14.7
2	1700	12.9
1	2144	11.3*

Nullet (1990) found that soil temperatures above 500 to 700 m in elevation on Maui were isothermic (i.e., had a mean annual temperature (MAT) less than 22 °C, greater than 15 °C, and smaller than 5 °C summer/winter difference) at 50 cm depth in the soil. In Hawai‘i, severe changes in temperature with season do not occur. In many areas, the diurnal variation in temperature exceeds or is at least equal to the change in temperature throughout the year (Sato 1973). This could affect $\delta^{13}\text{C}$ values throughout the day.

As shown in Figure 7, the effect of temperature on the $\delta^{13}\text{C}$ values of the DIC in our study area is negligible because the mean annual temperature range is so small (11 to 20 °C, or 284 to 294 K) (Sanderson 1993). The greater the influence of atmospheric CO_2

and the greater amount of C₄ ground cover, the heavier the δ¹³C values of the DIC will be. There is a ~ -1.7‰ change from the coolest temperature to the warmest at 0% C₄ and atmospheric mixing; the largest differences in δ¹³C value would be seen under these conditions. These calculations also apply to soil temperatures, which fit into the temperature ranges used.



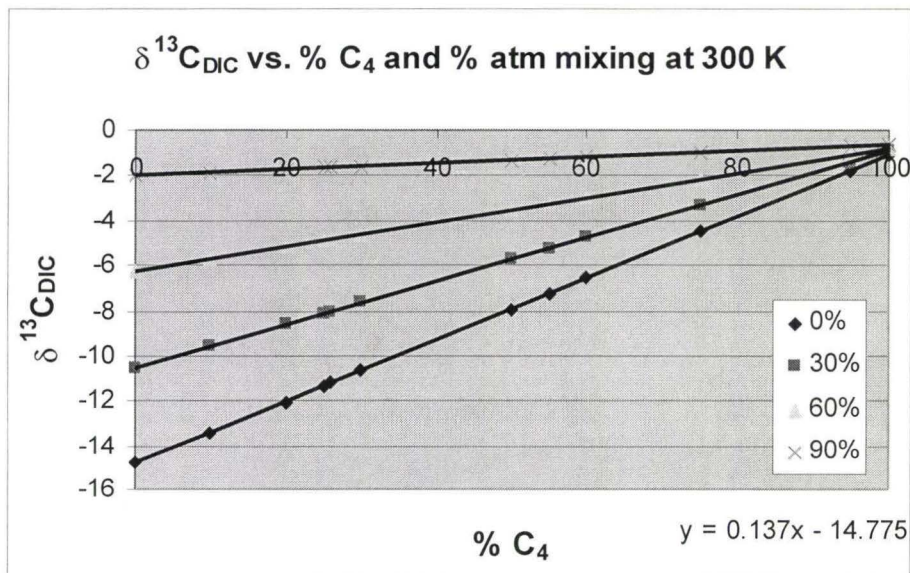
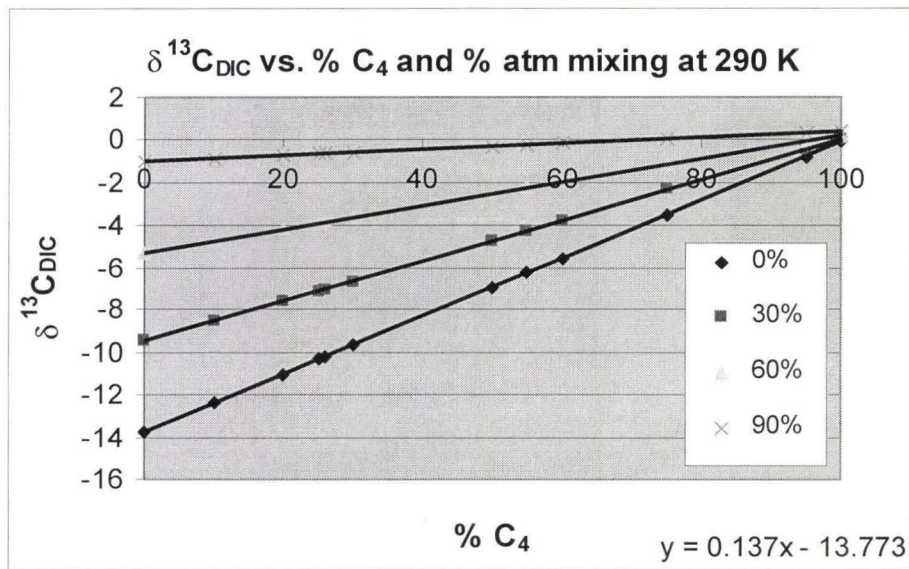


Figure 7. How $\delta^{13}\text{C}$ values of DIC would change with varying amounts of C_4 plant ground cover and atmospheric mixing at a pH of 7.8 at different temperatures (expansion of calculation in Cerling 1984). As in Cerling (1984), the C_4 endmember $\delta^{13}\text{C}$ value was taken as -8.5‰ ; C_3 $\delta^{13}\text{C}$ was -22.2‰ ; but atmospheric $\delta^{13}\text{C}$ in CO_2 was the current value of -8‰ , as opposed to -6‰ . Equations are for 90% atmospheric mixing (y-intercept is $\delta^{13}\text{C}$ value at 0% C_4).

$\delta^{13}\text{C}$ values from -22 to -12‰ have been reported in DIC in Hawai‘i (Hufen 1974; Voss 1994). DIC in the HSDP freshwater aquifer was dated to 2200 years B.P. and had an average $\delta^{13}\text{C}$ value of -12‰, 8‰ heavier than the -20‰ value of the Pearl Harbor freshwater aquifer on Oahu. The difference in the values found in these two Hawaiian groundwater bodies could be due to the values of CO_2 dissolved in the recharging water as it passes through the atmosphere and soil horizons, the dissolution of carbonate materials within the aquifer, and the deposition of carbonate minerals in the aquifer (Boutton 1991a).

The heavier $\delta^{13}\text{C}$ values in the HSDP aquifer compared to Pearl Harbor waters is most likely not due to diagenesis within the aquifer. Buried organic carbon (-22‰) would move the $\delta^{13}\text{C}$ value to lighter values, not heavier values. Calcite deposition would also make the $\delta^{13}\text{C}$ value lighter. If marine calcite (0‰) were to form within the aquifer during submergence of the volcano 140,000 years ago, its dissolution could possibly shift the values; however, very little indication of calcite was found in the HSDP core and it is therefore taken as unlikely that it formed upstream of the flow path. Furthermore, a large proportion of the $\delta^{13}\text{C}$ value (40%) would have to be attributed to calcite to change the $\delta^{13}\text{C}$ value to the values found, and since the calcite would be at ~140,000 years old, the radiocarbon age of the DIC would shift to an older age than that found (Thomas 1996). Sulfate reduction could also change the $\delta^{13}\text{C}$ value of the DIC, however, none of the products of sulfate reduction (sulfite) was found in the borehole waters (Thomas 1996). Therefore, the $\delta^{13}\text{C}$ value found in the DIC of the aquifer is most

likely a result of the $\delta^{13}\text{C}$ value of the soil gas and also possibly the atmospheric CO_2 that dissolved in the recharging water, assuming no diagenesis occurred during its trip from the recharge zone to the borehole (Thomas 1996).

All sampling sites are located in regions of the island where rainfall exceeds moisture demands (Sanderson 1993). Average rainfall ranges from approximately 1000 mm to 5100 mm per year, decreasing with elevation along the transect (Giambelluca 1986). Rainfall averages were near normal or above for most of the study period. The last sampling period (January 2003) was drier than usual (NOAA 2004).

Current vegetation in pasture areas consists mostly of the C_4 grass kikuyugrass (*Pennisetum clandestinum*), with clumps of the C_3 grasses Yorkshire fog (*Holcus lanatus*), orchardgrass (*Dactylis glomerata*), perennial ryegrass (*Lolium perenne*), Kentucky bluegrass (*Poa pratensis*), sweet vernalgrass (*Anthoxanthum odoratum*), and meadow ricegrass (*Microlaena stipoides*) (Mathews 2003), while in forested areas the major vegetation are C_3 plants such as ohi'a trees (*Metrosideros polymorpha*), koa trees (*Acacia koa*), and hapu'u ferns (*Cibotium glaucum*) (Townsend 1995).

3.2 VISITS, TRIPS, AND NUMERATION

A 'visit' constitutes a sampling of an area. The first visit to an area and site was given a number (e.g. "Site 1"); alphabetical suffixes were appended to the site number to distinguish first visit samples from subsequent samples ("Site 1A"). The alphabetical labels ("A", "B", etc.) were not necessarily collected during the same trip (e.g., 1A was

not collected during the same trip as 2A). Sample numbers accumulated throughout the project, and at no point did the sample counter restart. A preliminary trip to the Island of Hawai'i was made at the end of March 2002. During this trip, potential sites and areas were selected according to their elevation and accessibility. Samples 1 through 20 were collected from Areas 1 and 3 during this trip.

Another trip was made in April to collect the first samples from all sites. Areas 3, 4, and 5 were visited and Area 1 was resampled. In mid-June, all areas were resampled and Mauna Loa and western Mauna Kea were sampled. Sample suites 3 and 4 were taken in October 2002 and January 2003, respectively, and Nobriga Ranch (Area 2) was added to the transect during these sampling periods. In April 2003, vegetation was sampled from Areas 1, 4, 6, as well as similar elevations with different vegetation on Mauna Kea and Mauna Loa. Soil samples were taken of the upper pastureland to analyze the $\delta^{13}\text{C}$ values of the organic material in this area in August 2003.

Several difficulties were encountered during sampling. In rocky areas, it was difficult to duplicate depths at each visit. Sample bags were limited during the third trip and a few sites (4A, 20A, 21A) had to be abandoned in order to conserve bags. An effort was made to obtain representative samples from each area and across the transect in spite of these setbacks. Area 2, Nobriga Ranch, is privately owned was not available for early sampling trips.

Rainfall in the Transect

No rain gauges are situated in the upper part of the transect. The closest gauges are in Hilo and Piihonua, where Area 5 is located. All information is based upon the rainfall totals available from those gauges. The wettest month in the portion of the Island of Hawai'i that contains the transect is usually March. In March 2002, even though this area received greater than 10 inches of rain, it was still below normal. April 2002 continued to have less than normal amounts of rainfall, although most gauges had normal year to date totals. Near to above normal rainfall for the year continued through the summer of 2002. September received near to above normal rainfall on the windward side. In October, which marks the beginning of the rainy season in Hawai'i, the gauges only recorded 40% of normal rainfall. November was also unusually dry. Overall, 2002 received normal amounts of rainfall, although this was mainly due to very wet conditions earlier in the year, as El Niño conditions made the end of the year drier than normal. January 2003 continued in the dry trend, with 15% of normal rainfall (NOAA 2004).

3.3 AREAS AND SITES OF THE TRANSECT

Area 1

Area 1 is located at approximately 2100 m elevation, in pastureland currently used for cattle ranching. Its soil is rocky and brown and vegetation consists of grasses and gorse scrub bushes, as well as a few stands of dying koa trees. The area is hilly and in the vicinity of numerous cinder cones. However, it is often misty and overcast and

rain of any significant quantity is rare. The soil is thin in many places and often several attempts had to be made in order to penetrate the soil to a sufficient depth due to the soil's rocky nature.

Sampling area 1 is located in the Puu Oo and Pua Akala quadrangles, and is in the Hanipoe-Maile-Puu Oo soil association. These soils are found from 762 to 2440 m on the Island of Hawai'i and are well-drained with medium to moderately fine subsoil that formed from volcanic ash. These areas receive 76 to 300 cm of rain every year. The mean annual soil temperature is between 12 and 17 °C. Ohia, koa, naio, mamane, tree fern, rattail, brome fescue, kikuyugrass, and orchardgrass make up the vegetation in areas with these soils (Sato 1973).

More specifically, many soils in the highest elevation are Laumaia silt loams (LUC, LAD). These soils are located from 1675 to 2440 m on Mauna Kea, have a mean annual soil temperature of 11 to 12 °C, and get between 89 and 178 cm of rainfall a year. Sweet vernal grass, Yorkshire fog, carpetgrass, and white clover are the main flora in the area (Sato 1973).

Site 1 (N 19° 43.840, W 155 21.330; 2040 m elevation) is located in a grassy area off of Mana Rd., an unimproved road off of Saddle Road on the Island of Hawai'i. The sample was taken at 38 cm depth during the first visit, and 61 cm during the second. During the third and fourth visits, initial sampling depth was resumed for all sites.

Site 2 (N 19° 45.911, W 155° 21.230; 2017 m) is positioned in a valley next to a large rock. Samples were taken at 56 cm deep within the soil there. Visit 2 to this area revealed that a small fire had taken place not long prior to our visit.

Site 3 (N 19° 45.906, W 155° 21.230; 2039 m) was also located in the incinerated area. Visit 2 (N 19° 45.834, W 155° 21.206; 2013 m) was not taken in this position, due to GPS difficulties. Site visitation was resumed at the original site after this anomalous visit. Samples were taken at a depth of 89 cm.

Site 4 (N 19° 45.470, W 155° 22.090; 2122 m) is along the roadside. Cows graze this area and the grass is shorter and healthier, but the ground is more hummocky and rockier. Gorse bushes are larger and more numerous at this site than the previous three sites. Samples were taken at 58 cm depth during the first visit to Area 1, but difficulties in sampling to a sufficient depth prevented subsequent sampling during Visit 2.

Samples were taken near a cattle guard at Site 5 (N 19° 43.820, W 155° 23.918; 2139 m). Dead gorse bushes, thick, long grass, and a stand of koa trees inhabit this site. Samples were taken at a depth of 66 cm.

Site 6 (N 19° 43.197, W 155° 26.144; 2197 m) is in close proximity to a cinder cone and the soil there is ashy, lapilli-like, dry, and coarse. The grass is short and several mamani trees are nearby. Samples were taken at 89 cm.

Area 2

Area 2 is in between Areas 1 and 3 in elevation, on Pu'u O'o Ranch land, known as Nobriga Ranch. Access to this area was restricted during early sampling periods. These pasturelands contained more stands of trees and the soil contained less cinder. Area 2 is also in the Puu Oo quadrangle and is associated with the Hanipoe-Maile-Puu Oo soils. Soils in this area are PUC or PND (Puu Oo and Piihonua silty clay loams). PUC soils are located between 1675 and 1981 m, receive between 165 and 254 cm of rainfall, and have a mean soil temperature of 11 to 13 °C. Ohia, alapaio fern, tree fern, koa, sweet vernal, and white clover vegetate these soils. PND soils are located from 1370 to 1981 m in elevation, get more than 228 cm but less than 381 cm of rainfall a year, and have a mean annual soil temperature of 12.7 to 14.4 °C. Natural vegetation on these soils include ohia, koa, alapaio fern, sweet vernal, and kikuyugrass (Sato 1973).

Site 39 (N 19° 42.637, W 155° 23.081, 1828 m) was located on a small hill. Samples were taken at 107 cm. Samples at site 40 (N 19° 42.949, W 155° 22.208, 1748 m) were taken beside a small, man-made pond. The area was heavily trafficked by cows. Samples at this site were taken at 71 cm. At site 41 (N 19° 42.726, W 155° 21.603, 1651 m), it was harder to pump soil air out, possibly due to clay layers. The soil was very deep and samples were taken at 91 cm. Site 42 (N 19° 42.413, W 155° 20.690, 1548 m) was in the middle of a pasture. Samples were taken at 99 cm. Samples from site 43 (N 19° 42.607, W 155° 20.670, 1555 m) were taken at 74 cm.

Forest/pastureland comparison sites:

Site 44 (N 19° 42.960, W 155° 19.798, 1471 m) was located beside a fenced-in forest. These samples were the control for forest/pastureland comparisons. Samples were taken at 97 cm.

Site 45 (N 19° 42.983, W 155° 19.810, 1470 m) was in a forest in the Nobriga Ranchlands. It contained hapu'u ferns, ohia, and native raspberry. Samples were taken at 99 cm.

Site 46 (N 19° 42.983, W 155° 19.810, 1470 m) was also within the forest, and seemed to contain clay layers interspersed with ash layers in its soil. Samples were taken at 102 cm.

Area 3

Areas 3 through 6 are all in the Akaka-Honokaa-Kaiwiki association of soils. This association is characteristically well drained and has moderately fine textured subsoil. These soils are found from sea level to 1830 m. These areas receive 200 to >508 cm of rain every year. The mean annual soil temperature is between 12 and 24 °C. Ohia, koa, tree fern, and false staghorn fern make up the vegetation in areas with these soils.

Sampling areas 3 and 4 are in the Upper Piihonua quadrangle. Soils are of the Kahaluu (rKAD) and Akaka (rAK) series, respectively. Kahaluu soils are well drained thin soils with pahoehoe bedrock. Their elevation is 1066 to 2133 m, rainfall ranges between 228 to 381 cm annually, and mean annual soil temperature is 12.7 to 13.8 °C.

Vegetation on these soils is ohia, tree fern, amaumau fern, uluhe fern, and puakeawe. Akaka soils, which are also Areas 5 and 6 soils, are moderately well drained silty clay loams formed in volcanic ash. The soils range from 304 to 1370 m in elevation, have 381 to 762 cm annual rainfall, and annual mean soil temperatures of 13.3 to 15 °C. Ohia, tree fern, koa, false staghorn fern, and amaumau fern make up the natural vegetation (Sato 1973).

Area 3 is near an old U.S.G.S. river gauging station. The Wailuku River runs just north of the area. The average elevation in this area is approximately 1300 m. Vegetation consists of ferns, koa, native ohi'a, hapu'u, raspberry trees, and other typical rainforest plants. The detritus is thick and often was deeper than the rod could penetrate. This area is wetter than in Areas 1 and 2 and the soil is very moist in many places.

Site 7 (N 19° 42.752 W 155° 18.403; 1331 m) is just off the trail, next to the river. Samples were taken at 107 and 102 cm, respectively. Site 8 (N 19° 42.738, W 155° 18.402; 1346 m) is located near the trail and an abandoned hunter lean-to. Samples were taken from this site at depths of 53 and 64 cm during the two visits. Site 9 (N 19° 42.698, W 155° 18.389; 1359 m) is more swampy and moist than the other sites in this area. Samples were taken at 81 and 102 cm depth. Vegetation is similar at all sites (as described in the previous paragraph), and the soil is organic-rich, deep, wet, and dark brown in color. Site 10 (N 19° 42.765, W 155° 18.401; 1350 m) is located near a grassy

hill in an area where the soil starts to become rockier. As a result, samples were taken at shallower depths than earlier samples—at 30 and 33 cm depth.

Area 4

Area 4 is located near another former U.S.G.S. gauging station at a lower elevation and in close proximity to the Wailuku River. This area has similar vegetation and rainfall characteristics as those at Area 3 but has an elevation of 1000 m. Site 11 (N 19° 43.101, W 155° 15.535; 1030 m) is located along an unmarked trail far in the rainforest. Samples were taken here at 91 cm depth. The remaining sites were established across the river. This area is an ohī'a forest with hapu'u ferns and koa trees; due to the dense canopy cover, GPS coordinates had to be taken along the river, and are assumed similar for all 3 sites. Samples were collected at sites 12 through 14 (N 19° 42.941, W 155° 16.203, 1050 m). Site 12 samples were collected from 91 cm; 13 from 76 cm; and 14 from 46 cm depth.

Area 5

Area 5 is found in the Piihonua quadrangle, while area 6 is located in the neighboring Akaka Falls quadrangle. Area 5 and 6 consist of Akaka soils (rAK), described above for Area 3 (Sato 1973).

Area 5 is positioned at 700 m elevation, near an old sugarcane field and above a natural spring in a forest. The area is mossy, grassy, and the soil is deep and easy to penetrate. Sites 15 and 16 (N 19° 43.678, W 155° 11.163; 700 m) have identical GPS coordinates due to thick canopy cover. Sites 17 and 18 (N 19° 43.720, W 155° 11.099;

685 m) also are grouped together in this way. They all exhibit similar vegetation and soil conditions. Site 15 samples were taken at 99 cm and 102 cm depth. Site 16 samples were taken at 61 cm. Site 17 samples were taken at 104 cm, site 18 samples at 61 cm, site 17 samples at 102 cm, and site 18 samples at 61 cm deep in the soil.

Area 6

Area 6 is at a similar elevation as Area 5, but is located off the paved Kaiwiki Rd., a residential area. The soil is wetter and possibly more disturbed than in Area 5. The soils are Kaiwiki silty clay loam, which are well-drained and receive 381 to 508 cm of rainfall per year. This soil is located from 244 to 457 meters elevation on Mauna Kea. Mean annual soil temperature is 21 °C (Sato 1973). Hilograss, ohia, tree fern, californiagrass, and wainakugrass make up the native vegetation. This soil is mainly used for sugarcane. Sites 19 and 20 ('Upper Kaiwiki') (N 19° 45.648, W 155° 10.140; 682 m) and sites 21 and 22 ('Lower Kaiwiki') (N 19° 45.530, W 155° 09.473; 575 m) were established in this area. Site 19 samples were taken at a depth of 104 cm; site 20 samples at 61 cm. Sites 20 and 21 were omitted during the second visit in order to conserve sample bags. Site 21 samples were taken at 102 cm depth; site 22 samples were taken at 61 cm.

Non-transect areas

Similar elevations were sampled on western Mauna Kea and on Oahu, Hawai'i for comparative purposes. These sites were Areas 7 and 8, respectively.

Western Mauna Kea--Area 7

Area 7 is at approximately 2300 m and in a mamani and grassland forest. Western Mauna Kea is the leeward side of the mountain and therefore lies in the rain shadow of Mauna Kea. As a consequence, this area does not receive large quantities of rain and the soil is dry and fine. Site 23 (N 19° 48.983, W 155° 35.630; 2309 m) samples 55 and 56 were taken at 86 cm near a stand of trees; site 24 (N 19° 49.955; W 155° 35.589; 2317 m) samples 57 and 58 were taken at 99 cm in a grassy area; site 25 (N 19° 49.226, W 155° 36.536; 2041 m) samples 59 and 60 were taken at 107 cm near a dying tree; site 26 (N 19° 49.231, W 155° 36.486; 2053 m) samples 61 and 62 were taken at 61 cm in a grassy area; and site 27 (N 19° 47.984, W 155° 37.983; 1692 m) samples 63 and 64 were taken at 97 cm in an overgrown area.

Oahu--Area 8

Samples on Oahu, Hawai'i, were taken on Tantalus, a ridge in Honolulu, in December of 2002. Tantalus reaches a height of approximately 600 m. As these samples were used for comparison purposes, no GPS measurements were taken. Four sites were sampled at a range of depths (34-65 cm).

Diurnal/Nocturnal Samples

An air-tight, automatic pump was obtained for sampling over 12 hour periods, i.e., diurnal and nocturnal runs. Diurnal runs were started when the sun rose, and ended

when the sun set, at depths from 60 to 120 cm. Similarly, nocturnal runs commenced and concluded according to solar position. Samples were collected over several days.

Vegetation Samples

Vegetation samples were obtained from several sites in April 2003 in order to compare their $\delta^{13}\text{C}$ values to soil gas $\delta^{13}\text{C}$ values. Sites 1 through 6, 12, 13, 19, an area on Mauna Loa Strip Rd. (~1500 and 1300 m elevation) with koa trees, and an area on Mauna Kea with more natural vegetation (i.e., not available for cattle grazing but similar elevation) were sampled. The samples were dried and stored in sealed plastic bags until they could be powdered, weighed, and run in the Carlo Erba NC2500 Elemental Analyzer (EA). An effort was made to keep the relative proportions of species (by mass) representative of each site.

Soil samples

Soil samples also had to be taken in order to complete the picture of what was happening in the recharge zone (Area 1). The upper area was sampled in Sites 1 through 3 at different depths in August 2003.

3.4 MATERIALS AND METHODS

Soil gas sampling was conducted using a 109 cm stainless steel tube (O.D. 5 mm; I.D. 4mm), a peristaltic pump, Tygon rubber tubing, and 1 L SKC Tedlar bags. In order to block soil entry into the tube, a rivet was placed in the lower opening of the tube

before it was inserted into the soil. The tube was pulled up approximately one inch to dislodge the rivet and allow a space for soil air to enter the tube. Rubber tubing was connected from the tube to the hand pump and from the pump to the Tedlar bag. Tubing was secured around the tube by a hose clamp (Figure 8).

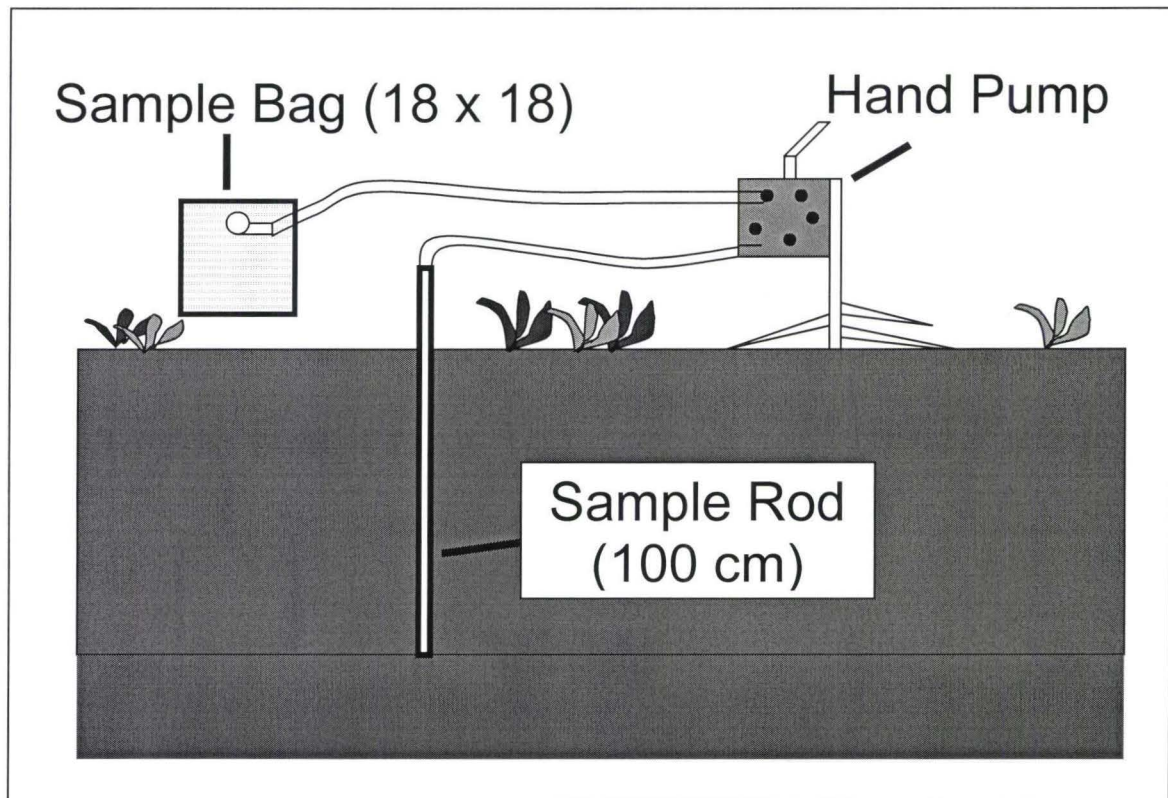


Figure 8. Schematic of soil gas sampling set up. A sample rod is placed in the ground and connected to a peristaltic pump, which is connected to a sample bag.

Ambient air was flushed out of the pump and tubing before connecting the sample bag to the system, and sample bags were flushed twice before the final sample was collected. Depth within the soil was measured with a tape measure once sample collection was complete. Bags were labeled with the area, site, sample number,

elevation, depth in the soil, GPS coordinates, and date and time. An effort was made to collect samples at a range of depths (30 to 104 cm) and conditions (vegetation/soil type/environment) in each area. Sample depth and time of day as previous visits was attempted during every subsequent visit. Two samples were collected per site per visit. Visits were made over a year in different stages of the year (January, April, June, and October) to determine seasonal site variability.

The transect consisted of 6 areas approximately 300 m apart in elevation, from 600 m to 2100 m; two of these areas were located at similar elevations but were agriculturally distinct in their histories. Each area contained at least 4 sites; site selection and depth of sample were based on available thickness of soil and area variability.

Sample bags were transported for analysis from the Island of Hawai'i to Oahu by commercial plane. Bags were stored in the passenger cabin during the flight to reduce the effects of pressure fluctuations.

Samples were analyzed on a MAT 252 Mass Spectrometer, online with a gas chromatograph with a Poroplot Q column. Several bags were kept and periodically tested to ensure storage integrity. Sample bags were attached to the gas chromatograph using a small piece of tubing and squeezed to introduce sample. Several aliquots of sample gas were run through the gas chromatograph before loading the final sample in order to reduce ambient air contamination. Sample loops varied from 3 to 250 μL , depending on CO_2 concentrations, and the contents of several bags had to be diluted in order to reduce the CO_2 concentrations for accurate analysis. In order to check the accuracy of dilutions,

several runs of a previously run sample bag were analyzed using the dilution method. A new Poroplot Q (0.32 mm inner diameter x 25 m) column was used in the oven, which was set at 35 °C. Samples were run against a UH3A-CO₂ standard with a $\delta^{13}\text{C}$ value of -31.915. Each sample bag was analyzed until $\delta^{13}\text{C}$ values were consistent within 0.5‰ for at least three runs. Runs took 700 seconds each, with standard introduced at 100 and 650 seconds. Sample peaks emerged at approximately 400 seconds.

Dilutions were performed with 20 mL combusted glass vials flushed with helium and capped with septa. Foil was added for mixing purposes. A 500 mL gas tight syringe was used to pierce the septa on the sample bags and collect the sample for injection. The syringe was purged twice before sample collection. At least three vials per bag were used in the dilution process. Once the syringe was purged and the final sample was collected, the syringe was placed into the vial and a venting needle was placed in the vial for escaping helium and reduction of pressure. Ten mL of sample were introduced into the vial. Needles were removed, and vials were then marked and labeled with a sample number. The vials were shaken for 1-2 minutes and allowed to equilibrate for at least another 15 minutes. After equilibration, a few milliliters of de-ionized water were introduced into the vial to create pressure and force the gas through a needle into the sample loop of the injection valve. Once pressure was relieved from the vial and the sample was loaded, the sample was injected into the gas chromatograph. Vials were analyzed within 10 hours in order to avoid contamination by ambient air. Average standard deviation (precision) of all 672 soil gas $\delta^{13}\text{C}$ values was +/- 0.19‰, which is

exceptional considering that the samples were run until three values within 0.5‰ of each other were obtained. The accuracy and precision of the GC for the samples is approximately 2‰, while the external precision for the mass spectrometer for CO₂ is 0.1‰.

Vegetation Samples

Vegetation samples were dried, powdered, weighed, and run in the Carlo Erba NC2500 Elemental Analyzer (EA) coupled with a Delta-Plus mass spectrometer in the Stable Isotope Laboratory at the University of Hawai‘i at Manoa. Standard reference material was acetanilide (71.02% C; 10.36% N). Eight standards of different weights were run throughout the sample runs. External precision for isotope ratios in the EA is 0.15‰ for both ¹³C/¹²C and ¹⁵N/¹⁴N. External precision for elemental concentration is 2‰ for carbon and 1‰ for nitrogen. Accuracy is normally +/- 0.2‰ on the EA.

Soil samples

Root and bulk analyses were taken per sample bag. Roots were picked out from each sample bag and run separately from bulk soil samples. Both were prepared in a similar manner as vegetation samples (described above).

Calculation of the $\delta^{13}\text{C}$ value of DIC

To calculate the $\delta^{13}\text{C}$ of the DIC, it was assumed that: magmatic CO₂ does not contribute to the $\delta^{13}\text{C}$, no carbonate or other diagenesis occurs in the aquifer; there are ideal conditions (i.e., molality is equal to activity at low salinities); soil gas was the source of the $\delta^{13}\text{C}$ value. An rough estimate of soil temperature can be found by adding

two degrees to the mean annual air temperature, as soil temperatures are usually two degrees warmer than air (Niemeyer 2003).

K_1 for freshwater at different temperatures can be calculated by the following equation:

$$(3) \quad pK_1 = \frac{3404.71}{T} + 0.032786(T) - 14.8435,$$

where T is in Kelvins (Mook 2001).

After K_1 is found, it may be used to find the species ratio $\frac{[HCO_3^-]}{[H_2CO_3]}$. K_1 is equal to the concentration of bicarbonate times the hydrogen concentration, divided by the carbonic acid concentration:

$$(4) \quad K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

It follows that the species ratio is equal to K_1 divided by the hydrogen ion concentration. Therefore, the ratio is equal to 10^{-pK_1} divided by 10^{-pH} . This is only applicable to solutions where the pH is less than ~10, and bicarbonate or carbonic acid is the major species (Clark 1997). In the 320 m deep HSDP freshwater aquifer, the salinity is near 0 and the pH is ~7.8 (Thomas, 1996). From the ratio, it is assumed that molality (m) is equal to activity at low salinities, and H_2CO_3 is counted as the same species as dissolved CO_2 (Clark 1997). To get the relative proportions of each component ($mHCO_3^-$ and $mCO_{2(aq)}$), the total DIC is set to 1:

$$mHCO_3^- + mCO_{2(aq)} = 1$$

$$(5) \quad m\text{HCO}_3^- = 1 - m\text{CO}_2(\text{aq})$$

where m is mole fraction of total DIC. So then,

$\frac{1 - m\text{CO}_2(\text{aq})}{m\text{CO}_2(\text{aq})}$ is equal to the species ratio, and can be normalized to find the

percentages of $m\text{CO}_2(\text{aq})$ and $m\text{HCO}_3^-$:

$$m\text{CO}_2(\text{aq}) = \frac{1}{1 + \frac{1 - m\text{CO}_2(\text{aq})}{m\text{CO}_2(\text{aq})}}$$

$$(6) \quad 1 - m\text{CO}_2(\text{aq}) = m\text{HCO}_3^-.$$

The mole fraction of each species in this calculation was verified by CO2SYS, using inputs for pH, pCO₂, temperature, and pressure. It matched with the results of the above calculation exactly. Accuracy for K₀ is within 0.2 to 0.5%, precision for K₁ is 0.5%, and K₂ is 0.7% (Lewis 1998).

From this point, it is necessary to calculate the fractionation factors (ϵ) between CO₂ (g) and CO₂ (aq) and between CO₂ (g) and HCO₃⁻. These fractionation factors are temperature dependent (Zeebe 2001). From CO₂ (g) to HCO₃⁻,

$$(7) \quad \epsilon = \frac{9483}{T} - 23.89\text{‰};$$

from CO₂ (aq) to CO₂ (g),

$$(8) \quad \epsilon = \frac{-373}{T} + 0.19\text{‰},$$

where T is in Kelvins. Providing the soil gas $\delta^{13}\text{C}$ value has been measured, everything necessary to calculate the $\delta^{13}\text{C}$ value of DIC is known. Using the isotope mass balance equation:

$$(9) \delta^{13}\text{C}_{\text{DIC}} = m\text{HCO}_3^- (\delta^{13}\text{C}_{\text{soil gas}} + \epsilon_{\text{CO}_2\text{g-HCO}_3^-}) + m\text{CO}_2(\text{aq}) (\delta^{13}\text{C}_{\text{soil gas}} + \epsilon_{\text{CO}_2\text{aq-CO}_2\text{g}})$$

the $\delta^{13}\text{C}$ value of DIC or soil gas may be calculated (Clark 1997).

For this project, the value of $\delta^{13}\text{C}$ of DIC is -12‰ (Thomas 1996). The corresponding, calculated $\delta^{13}\text{C}$ value of the soil gas in the recharge area for this water 2200 years ago is -21‰, using a pH of 7.82 (from borehole water data) and a temperature of 12.78 °C (286 K) from soil temperature calculations. Approximately 2200 years ago, atmospheric $\delta^{13}\text{C}$ values were roughly 1.5 to 2 per mille heavier than today, due to the addition of light $\delta^{13}\text{C}$ values from the burning of fossil fuels occurring in recent times (Indermuhle 1999). Plants using atmospheric air then would have an average $\delta^{13}\text{C}_{\text{DIC}}$ value 2‰ heavier than plants using atmospheric air today. Therefore, all other factors being equal, the soil gas value of -21‰ is 2‰ heavier than by today's standards. The same plants today would respire a value of -23‰.

CHAPTER 4 RESULTS AND DISCUSSION

In this chapter, $\delta^{13}\text{C}$ values and CO_2 concentrations from soil gas samples are presented and examined for trends. These results are then evaluated in the context of environmental processes described in the literature.

4.1 TRENDS IN $\delta^{13}\text{C}$ VALUES WITH ELEVATION

Two populations in the $\delta^{13}\text{C}$ data are evident (Figure 9): a grouping of light $\delta^{13}\text{C}$ CO_2 samples observed at generally lower elevations and a heavier CO_2 grouping at higher elevations.

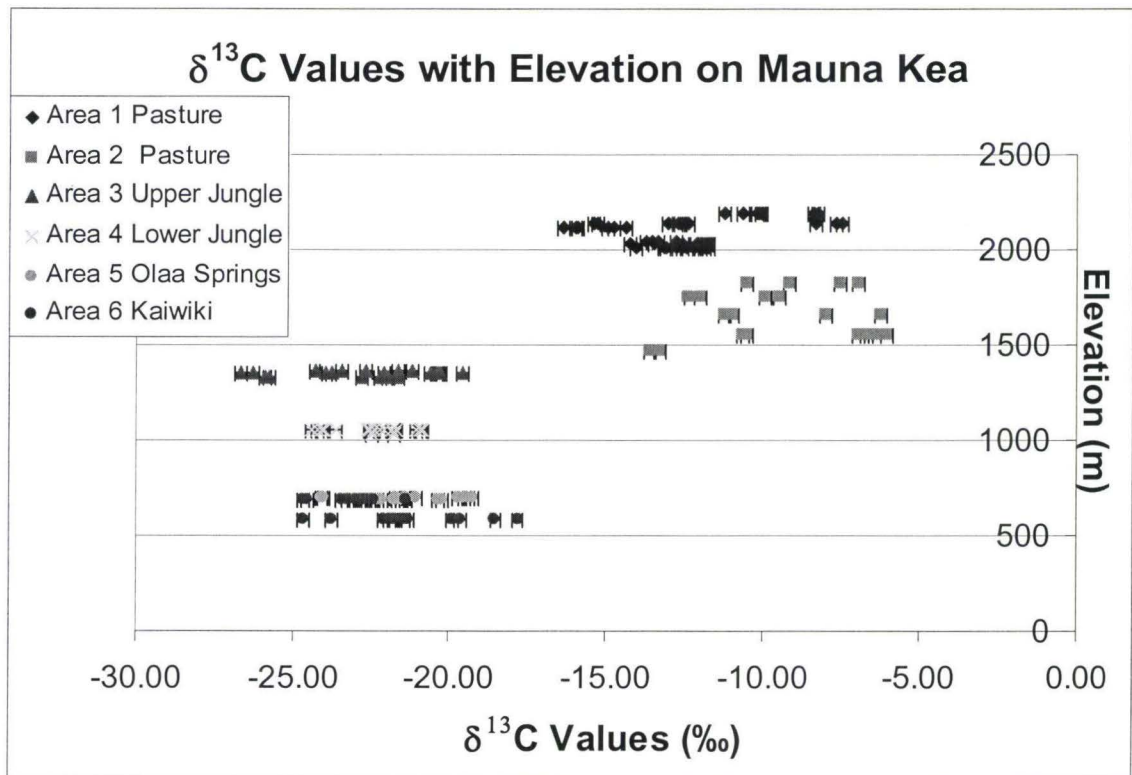


Figure 9. $\delta^{13}\text{C}$ values with elevation from all sampling periods on Mauna Kea. Standard deviation error bars are included for the six areas and are $\pm 0.2\text{‰}$. Two populations are clearly depicted: upper elevation sites (pasture) have $\delta^{13}\text{C}$ values enriched in ^{13}C , while lower elevations (forests) show more depleted values.

The Source of the Two Populations

Several factors may influence the $\delta^{13}\text{C}$ value with elevation, most notably, temperature, precipitation, and the assemblage of vegetation. In this transect, the temperature of the soil decreases roughly $10\text{ }^{\circ}\text{C}$, rainfall declines approximately 600 cm, and vegetation changes from forest to pasture with increasing elevation.

Moisture and temperature have been found to cause changes in the diffusion rate of ^{13}C out of the soil and the CO_2 production rate of plants, thereby affecting the $\delta^{13}\text{C}$

values. However, the amount these may affect the values is very small—on the order of a few per mille at most (Buyanovsky 1983; Dudziak 1996). In the transect, the average for the forest samples is approximately -22‰ (n = 261; standard deviation = ±2.44), whereas the average for pasture samples is -12‰ (n = 219; standard deviation = ±2.54). These two averages are significantly different. Temperature and moisture could not change $\delta^{13}\text{C}$ values by such a significant amount; thus, temperature and moisture cannot be the cause of the large 10‰ difference in $\delta^{13}\text{C}$ values between pasture and forest noted here.

A larger contribution from volcanic sources, higher contributions of atmospheric air, or a decaying pool of heavy soil organic matter in the pasture were also considered as possible sources for the heavy $\delta^{13}\text{C}$ values. However, each can be discounted as a probable source for the different $\delta^{13}\text{C}$ in the different groups as follows:

Magmatic CO₂: Mauna Kea volcano ended its shield-building phase of activity more than 100,000 years ago and the most recent alkalic stage eruption occurred ~5000 years ago suggesting that volcanic gas emissions as a source of heavy ^{13}C is unlikely.

Atmospheric CO₂: The atmosphere has a heavy $\delta^{13}\text{C}$ value (-8‰), but has a very low CO₂ concentration (0.036%), which enables us to determine the contribution of atmospheric CO₂ to the deep soil gas. If surface CO₂ is infiltrating into the soil in great amounts, CO₂ concentrations will be correspondingly small. CO₂ concentrations in the pasture range from 0.2% to up to nearly 6%. The concentrations were consistently greater than 2% in the majority of Area 1 samples, and no samples in Area 2 pasture had concentrations below 2%. In fact, Nobriga Ranch samples, which exhibited the heaviest

values, were upwards of 5% in many sites. Forest samples also had similar concentrations, which would not be the case if there were significant differences in the atmospheric infiltration of the pasture and forest. At the depths sampled, it is unlikely that the atmosphere would infiltrate into the soil in the amounts necessary for the change to occur.

Decay of recalcitrant soil organic matter: The decay of soil organic matter such as roots should take place over a short period of time—roughly 5-10 years (Gaudinski 2000). Root matter samples taken from depths of 46 to 116 cm in Area 1 (average $\sim -12\text{‰}$; $n = 5$; standard deviation = 0.9) reveal that the $\delta^{13}\text{C}$ value of the root matter is the same as the live roots are respiring, as shown in the soil gas samples. There was a high density of turgid, hydrated root samples at these depths, and their $\delta^{13}\text{C}$ values matched with the soil gas values sampled (Huang 2003). This indicates that the decay of young soil organic matter and the respiration from live roots are more likely the sources of the heavy CO_2 than the decay of recalcitrant soil organic matter.

Samples were taken in both the pasture and forest near the pasture-forest boundary in Nobriga Ranch to compare their respective values. Elevation, rainfall, and temperature were similar; the samples were taken a few hundred feet apart and within 30 minutes of one another. The only observable difference between the sites was vegetation. The forest-edge soil CO_2 samples had an average $\delta^{13}\text{C}$ value of -24‰ ($n = 12$; standard deviation = 0.10) and the pasture-edge samples an average $\delta^{13}\text{C}$ value of -13‰ ($n = 6$; standard deviation = 0.06). Additionally, the $\delta^{13}\text{C}$ values in the forested areas were

identical to each other, although they were as much as 600 m apart and had varying temperatures and amounts of rainfall.

That the $\delta^{13}\text{C}$ values are so different in an area where vegetation is the only variable, and so similar in areas where the only similarity is the vegetation, strongly suggests that the division in $\delta^{13}\text{C}$ values is due to the photosynthetic pathway of the major plant species (C_3 trees or C_4 grasses) living in these ecosystems. This conclusion is supported by the heavy $\delta^{13}\text{C}$ values of the root matter in the pasture and the high proportion of C_4 plants in pasture areas and C_3 plants in forests. Therefore, the more enriched, higher elevation population in Figure 9 is associated with pasture and the other with forest.

Trends Within the Two Populations

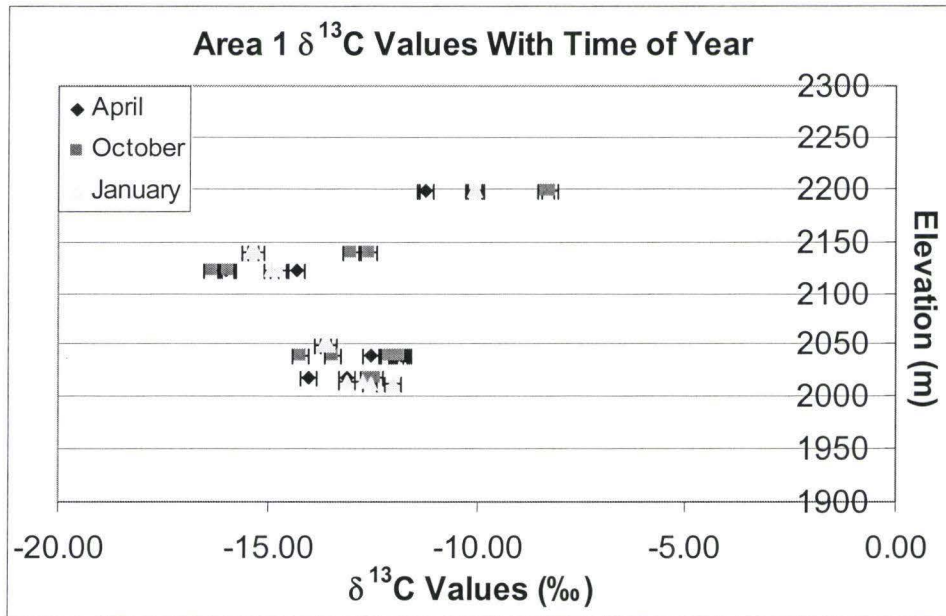
Since the values in the transect can be separated into 2 groups, the data were also analyzed for differences within those populations. The most obvious difference between the two pasture lands is the heavier values found in Area 2 versus Area 1. These two areas are statistically different, as determined by a heteroscedastic t-test within a 95% confidence interval (this test is used for all tests of significance, unless otherwise stated). The average $\delta^{13}\text{C}$ value in Area 1 is -12‰ ($n = 141$; standard deviation = 2.13) whereas Area 2 values average -9‰ ($n = 66$; standard deviation = 2.33). $\delta^{13}\text{C}$ values in the pastures, shown in Figure 10, seem to trend toward heavier values with decreasing elevation.

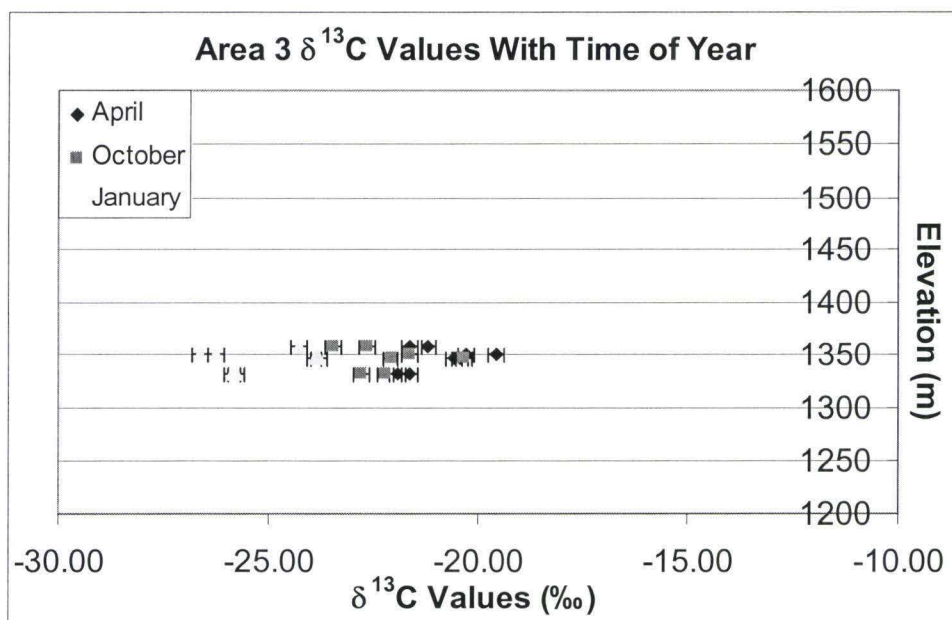
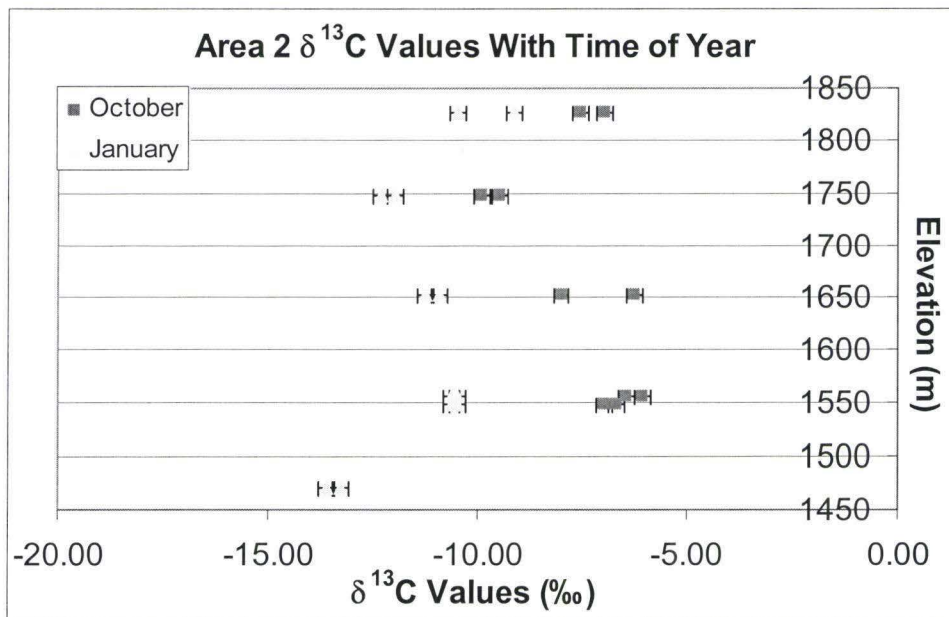
The same possibilities for the cause of forest/pasture land variations were considered for the difference between the two upper areas. Higher infiltration of atmospheric air, assemblage of plants, differences in temperature and moisture, volcanic sources, and soil organic matter were all considered possible causes for the differences seen. The same logic eliminating the volcanic, soil organic matter, and higher atmospheric air infiltration as sources in the forest/pasture land argument still stands in this case. In Area 1, which exhibits lighter $\delta^{13}\text{C}$ values, CO_2 concentrations range from 0.2% to 5%. Area 2 has soil gas CO_2 concentrations from 2% to 6% in the soil gas, precluding an atmospheric influence as the source of the heavier values.

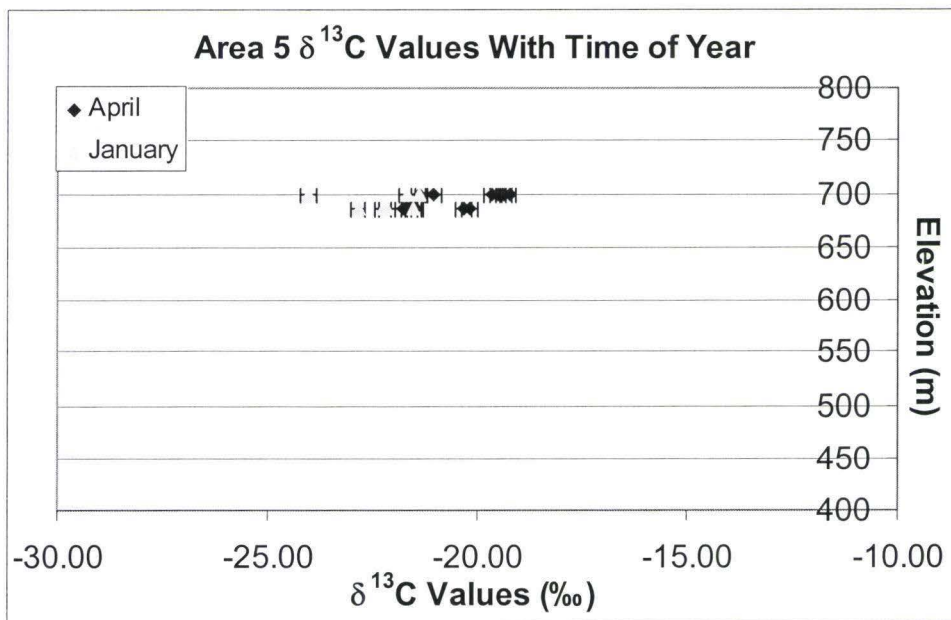
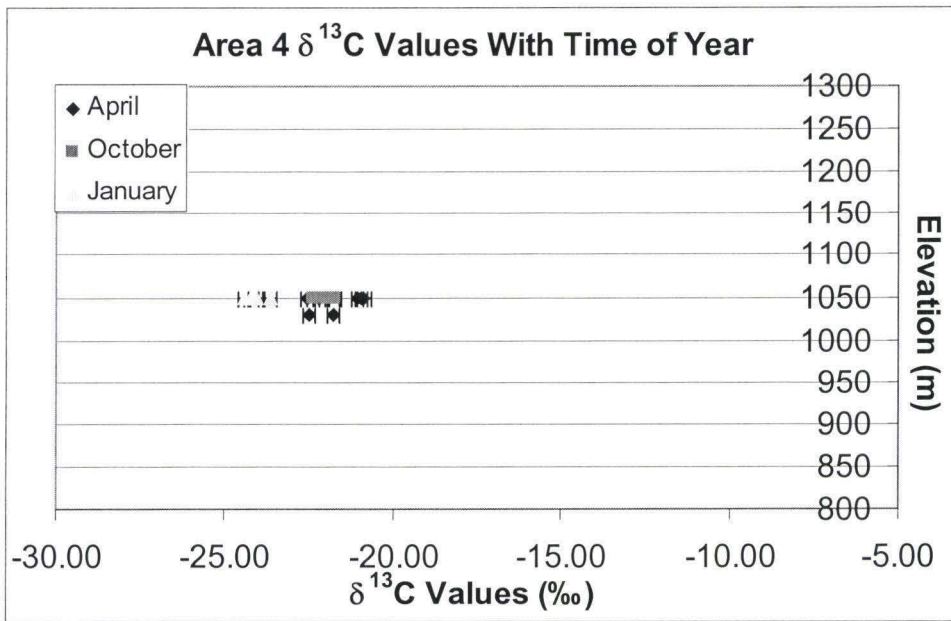
Temperature and moisture differences in this case vary much less between these two areas than within the whole transect—at most 2 °C and 150 cm of rainfall separate the two areas, which are 200 to 400 m apart in elevation. Higher rainfall and temperatures occur in Area 2, which is at a lower elevation than Area 1. Studies have shown that higher temperatures and moisture content in the soil leads to lighter $\delta^{13}\text{C}$ values (Dudziak 1996). This is contrary to the trend seen in this study; the lower elevation area, with higher rainfall and temperatures, exhibits heavier values in its soil gas.

Given the vegetative assemblages found in these areas, the trend toward heavier values is expected: Area 1 is a mixture of C_4 and C_3 grasses, whereas Area 2 should have fewer C_3 and more C_4 grasses, simply based on the temperature regimes at the two elevations. C_4 grasses grow optimally in warmer temperatures and have a maximum

elevation cutoff near the elevations in Area 1 (Mathews 2003). This study proposes a vegetative source as the cause for the heavier values in Area 2. Differences in forest $\delta^{13}\text{C}$ values with elevation are not apparent within the limits of error; average values for Areas 3, 4, 5, and 6 are as follows: -22, -22, -21, and -22‰ (Figure 10).







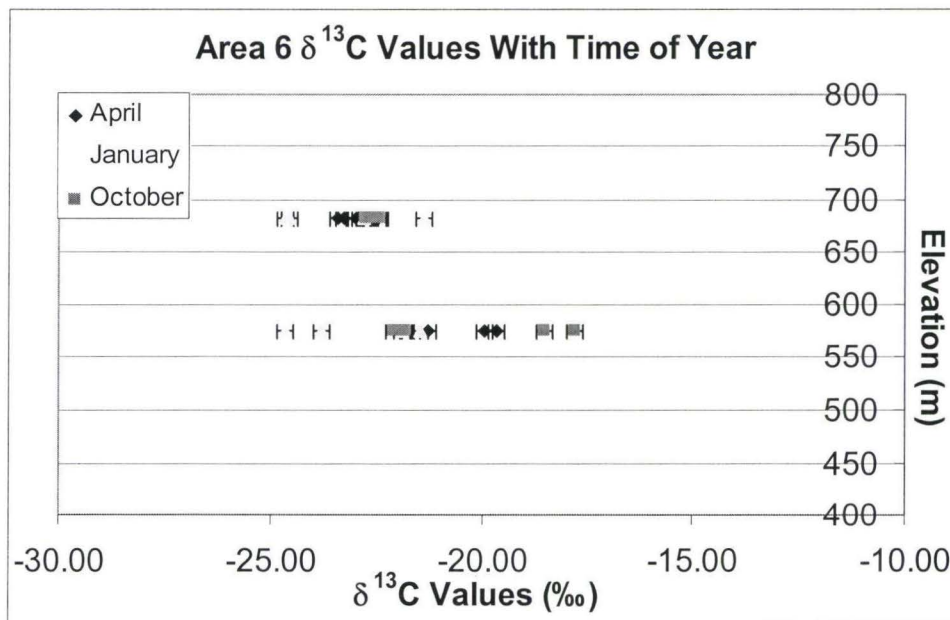


Figure 10. Average $\delta^{13}\text{C}$ values with elevation at each area with season. C_3 trees dominate the lower 4 sites, whereas the upper 2 sites are C_4 pasture. This accounts for the isotopic differences exhibited. Errors are $\pm 0.2\text{‰}$.

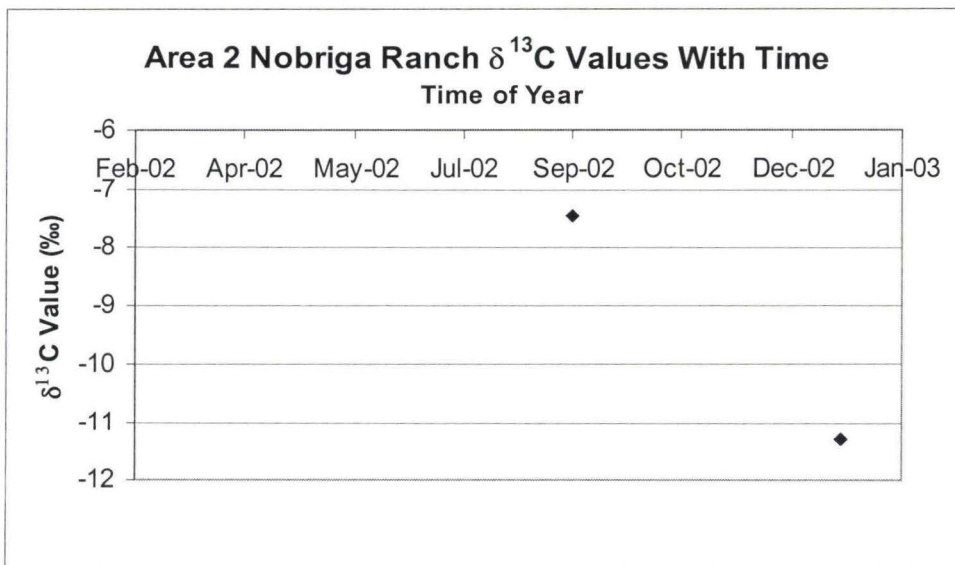
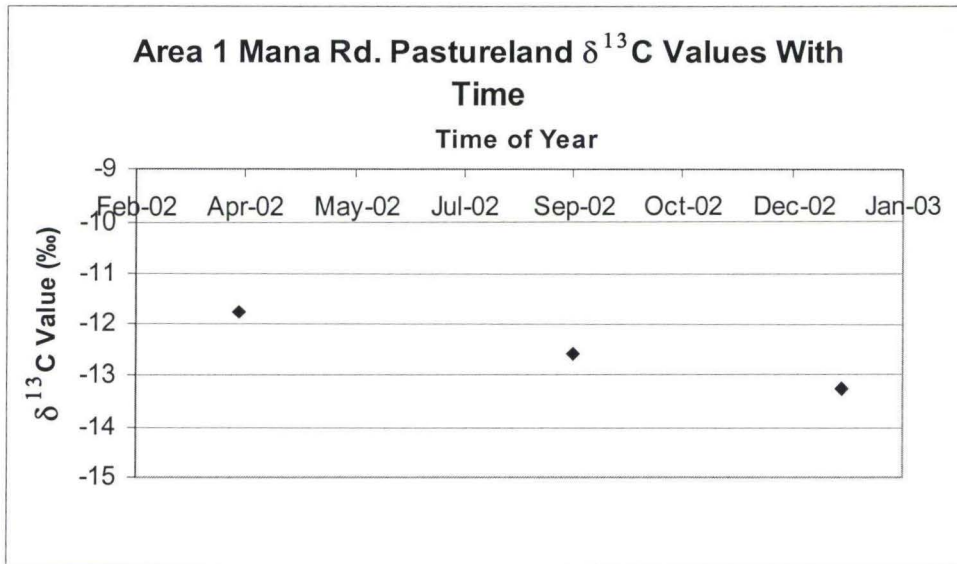
4.2 SEASONAL TRENDS IN $\delta^{13}\text{C}$ VALUES

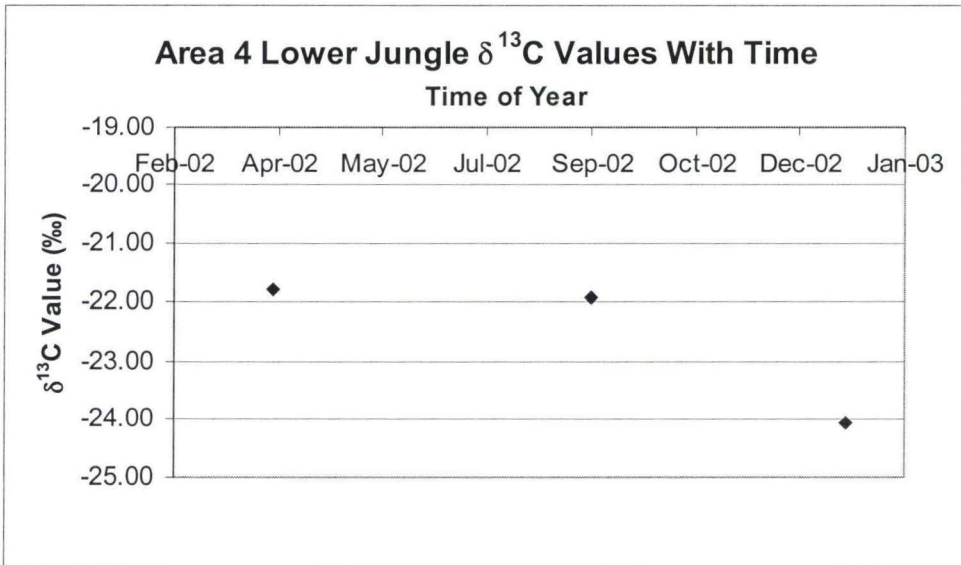
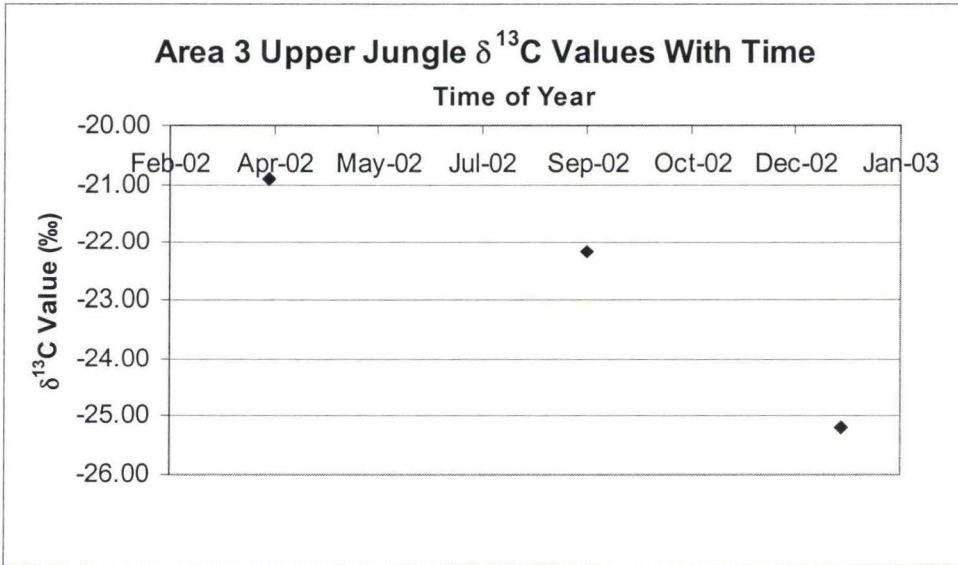
There are seasonal differences within each area (Figure 11). In this study, nearly all areas show a slight depletion in ^{13}C from April to October, and a much greater decrease from October to January. This result seems to contradict what is expected of vegetation during each season.

Normally, rainfall in the transect increases from summer to winter, with the winter also being called the rainy season. More moisture should lead to lighter values (Buyanovsky 1983; Dudziak 1996). During the period of sampling, the amount of rainfall actually decreased from summer to winter. This should lead to heavier values, due to the increased flux of ^{12}C to the atmosphere (Buyanovsky 1983; Dudziak 1996).

Summer growing seasons, with warmer temperatures and higher photosynthetic activity, should lead to the production of higher concentrations of CO₂ and lighter δ¹³C values (Dudziak 1996). However, the differences in summer/winter temperatures in Hawai‘i are not as great as those in temperate latitudes, where most studies have taken place. The moderate temperatures allow for a year-round growing season for many plants in Hawai‘i. The trend found in this study could be due to the changes in growth rates associated with each type of plant. C₃ plants grow optimally in cooler temperatures whereas C₄ plants are ‘warm season’ plants. All other factors being equal, it is expected that heavier values will be found during the summer, when C₄ plants are growing faster than C₃ plants, but winter temperatures (not being cool enough to stop production of CO₂ altogether) will allow C₃ plants to become dominant in terms of CO₂ production. This alternation of production is what is seen in this study. Soil gas CO₂ concentrations appear to support this hypothesis: although remaining relatively stable throughout the year, in the upper, C₄ dominated pasture soil CO₂ concentrations show a slight decrease and C₃ forestlands show a slight increase from September to January. Additionally, at Nobriga Ranch, samples taken from the forest/pasture boundary in January show that average CO₂ concentrations are higher in the forest (3.4%) than in the adjacent pasture (2.4%). Concentrations in the pasture are still high, and indicate production of CO₂ by roots or microbial activity, but perhaps the higher concentrations in the forest are indicative of an increase in activity there, or a decrease in activity in the pasture. Although contrary to other findings, the trend towards heavier values in summer shows

the importance of not relying on season alone to predict trends in $\delta^{13}\text{C}$ value in the tropics; rather, temperature and photosynthetic pathway are the key to predicting the source of soil gas CO_2 .





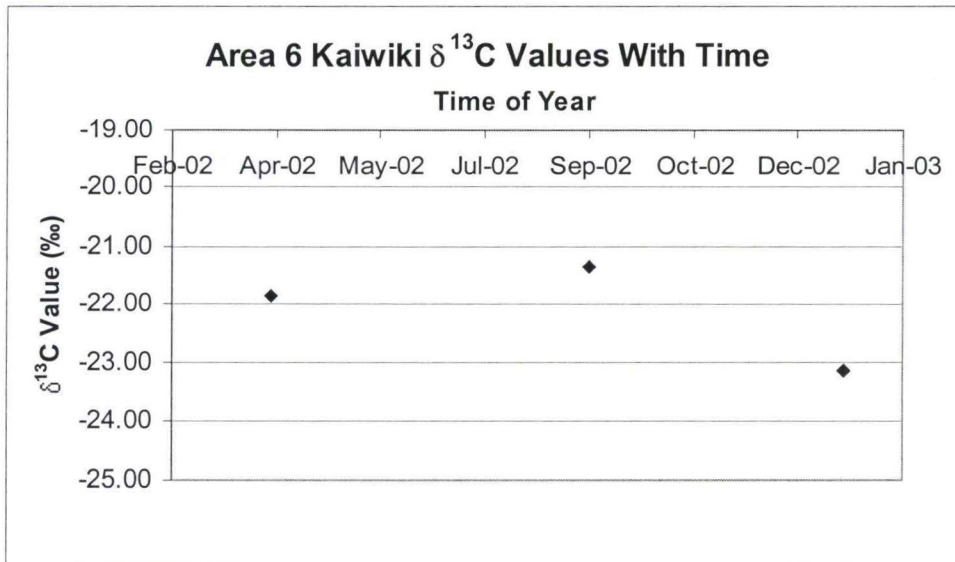
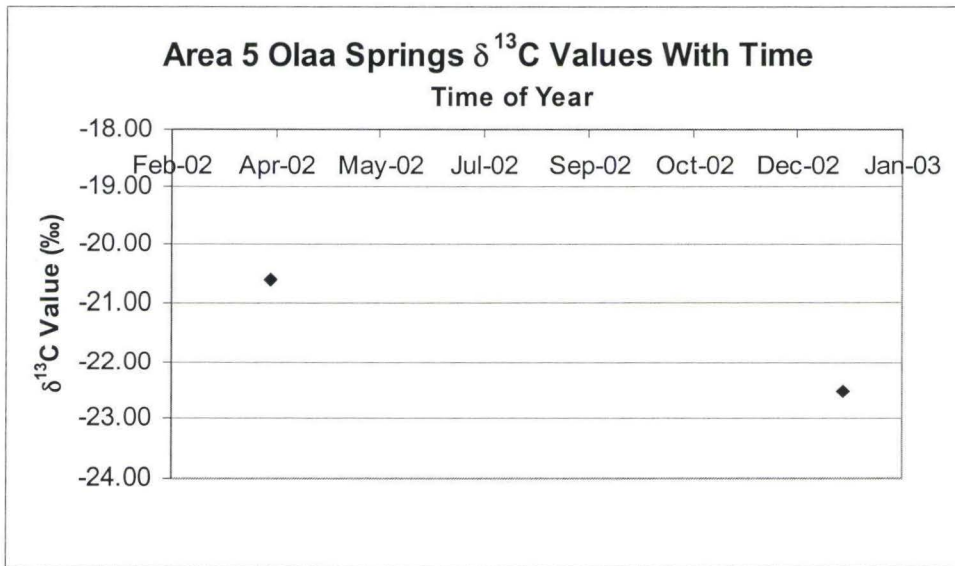


Figure 11. Average $\delta^{13}\text{C}$ values with time of year. Most show the greatest decrease in $\delta^{13}\text{C}$ value between September and January. This is possibly due to the greater activity of C_3 plants in the cooler temperatures at this time.

4.3 $\delta^{13}\text{C}$ VALUES AND CO_2 CONCENTRATIONS WITH DEPTH

Few trends of $\delta^{13}\text{C}$ values and CO_2 concentrations with depth were found in this study (Figure 12). An increase in concentration and $\delta^{13}\text{C}$ values with depth was

expected, but sampling was done at different depths for each site within an area, and could account for the absence of that trend. If samples were at different depths within the same profile, trends would be anticipated, although they are not always found (Andrews 1999; Hanson 2000). Several studies investigating soil gas samples at different depths within the same soil profile did not find a correlation between $\delta^{13}\text{C}$ value or CO_2 concentrations with depth. This finding was attributed to the differential contributions of microbial and root respiration with depth, and is a plausible reason that no correlation was found in this study (Andrews 1999; Hanson 2000).

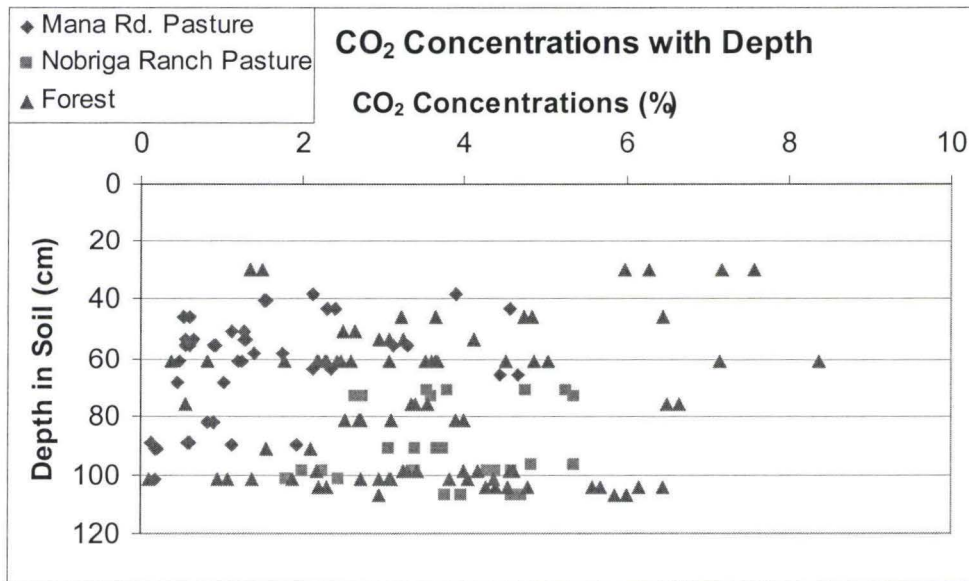


Figure 12. CO₂ concentrations with depth. No trends seem to exist. The highest concentrations were found in Nobriga Ranch (purple) and the forest (green).

Soil gas samples in burned portions of Area 1 were also taken; their $\delta^{13}\text{C}$ values are not significantly different from areas not cleared of grass. CO₂ concentrations, however, are an order of magnitude lower (0.05%) than the similar area with intact vegetation (0.6%). The fact that the $\delta^{13}\text{C}$ values are statistically similar, but the concentrations are lower, emphasizes the small impact atmospheric CO₂ fluxes have on soil gas $\delta^{13}\text{C}$ values in this area, as predicted for soil gas at these depths (> 60 cm). If the atmosphere were the cause of the lower concentration, the $\delta^{13}\text{C}$ values would reflect atmospheric values and be heavier. Therefore, the main source of the CO₂ is either microbial or live root respiration. The prescribed gorse burns (used to control the spread of the invasive, exotic gorse bushes) must reach temperatures of 100 °C for at least 15 minutes in order for the gorse seed to be killed. This amount of heat penetrates a half an

inch into the soil (Zabkiewicz 1978). The deep roots of grasses should survive this and produce some CO₂. Their contribution makes up the lowered CO₂ concentrations could indicate that microbial production of CO₂ is small or negligible. If the roots do not survive, the soil gas found in the burned areas is due to microbial breakdown of the dead vegetation. In that case, the difference in concentrations indicates that microbial contributions to the soil gas $\delta^{13}\text{C}$ value are similar to that of live roots, but respire less CO₂ to the soil atmosphere, making live roots the main source of CO₂ in this area.

4.4 DIURNAL/NOCTURNAL $\delta^{13}\text{C}$ VALUES AND CO₂ CONCENTRATIONS

Samples were taken over 12 hour periods (sunrise to sunset, and vice versa) at a depth of 78 cm to determine differences or patterns in nocturnal and diurnal $\delta^{13}\text{C}$ values and CO₂ concentrations (Figure 13). The average $\delta^{13}\text{C}$ value for nocturnal samples was -10‰ (n = 9; standard deviation = ± 0.2), whereas the diurnal average is -14‰ (n = 12; standard deviation = ± 0.7). These averages are significantly different within a 95% confidence interval. It is expected that heavier values are found at night because the reduction in root respiration during dark respiration (due to a decrease in temperature and photosynthetic activity) causes a decrease in CO₂ concentration, allowing atmospheric air into the soil. Lower root respiration at night could allow atmospheric air to infiltrate deeper into the soil profile and enrich the soil atmosphere in ¹³C, as well as decrease the CO₂ concentration. Concentration studies confirm that the source of the enriched CO₂ is the atmosphere; atmospheric concentration is around 0.03%. Diurnal concentrations

averaged 0.3%, which is an order of magnitude higher than atmospheric values. Nocturnal concentrations were 0.1%, roughly three times higher than atmospheric.

It is also expected that the differences between nocturnal/diurnal $\delta^{13}\text{C}$ values would be comparable to seasonal differences. Temperatures can be 7 °C lower at night than during the day at the elevations these samples were taken; average annual temperatures may only vary by 13 °C (NOAA 2004).

However, the CO_2 concentrations and $\delta^{13}\text{C}$ values reported above may not represent the actual values and concentrations. The method of acquiring these samples could introduce error into this study. The samples were collected by pumping air out from the soil at a constant rate over 12 hours. If the pumping rate was higher than the rate at which the CO_2 was created (after pumping out the existing pool of soil CO_2), it is possible that atmospheric air could have been drawn down into the soil, altering the sample data. However, since the pumping rate was constant throughout the day and night, the relative concentrations are comparable. In addition, the pump ran for roughly 10 minutes before sample collection started, in an effort to purge the sample tube and deplete the existing pool of CO_2 . Nocturnal samples were taken first, so even if the existing pool of CO_2 was not completely pumped out at the start of the nocturnal run, the higher concentrations and lighter values in the diurnal samples cannot be attributed to the existing pool. This further emphasizes the low rate of production during the night hours compared to daytime.

Seasonal samples show slightly higher, if not similar, concentrations (0.6%) as the diurnal samples analyzed. Seasonal samples have a $\delta^{13}\text{C}$ value averaging -15‰ for the same site during this period of time. The higher concentrations and lighter values in the normal sample show that although the $\delta^{13}\text{C}$ values and concentrations for the diurnal/nocturnal samples may have interacted with atmospheric air, the contamination is not extensive. The differences are not significant within a 99% confidence interval. The standard deviation for these numbers is $\pm 0.2\%$ for the nocturnal and diurnal $\delta^{13}\text{C}$ values, and $\pm 0.05\%$ for suite 4's site 4 $\delta^{13}\text{C}$ values (average standard deviation for soil gas $\delta^{13}\text{C}$ values for all suites is $\pm 0.2\%$).

Diurnal and nocturnal samples were also taken in burned areas for comparison purposes. As discussed earlier, the nearly 10-fold drop in CO_2 concentrations between non-burned and burned areas suggests that microbial production of CO_2 is, at most, a few percent of the total CO_2 production. Nocturnal samples averaged -11‰ ($n = 3$; standard deviation = ± 0.1), whereas diurnal values were -13‰ ($n = 6$; standard deviation = ± 0.2). This trend is similar to the one in the non-burned area, with enriched values during the daylight hours. Concentrations, however, are much lower than in non-burned samples (0.05% in nocturnal samples, 0.09% in diurnal). The absence of vegetation probably explains the difference in concentration levels. Roots probably survive the gorse burns and are able to produce CO_2 , although not as much as if the root and plants were intact.

The production of CO_2 by root and microbial respiration must be high enough to sustain typical $\delta^{13}\text{C}$ values, even at low concentrations. Standard deviation of the

analysis is similar to the standard deviation of $\delta^{13}\text{C}$ values taken in unburned areas. These data are also consistent with the conclusion that atmospheric CO_2 makes little, if any, contribution to the soil gas at the depths sampled.

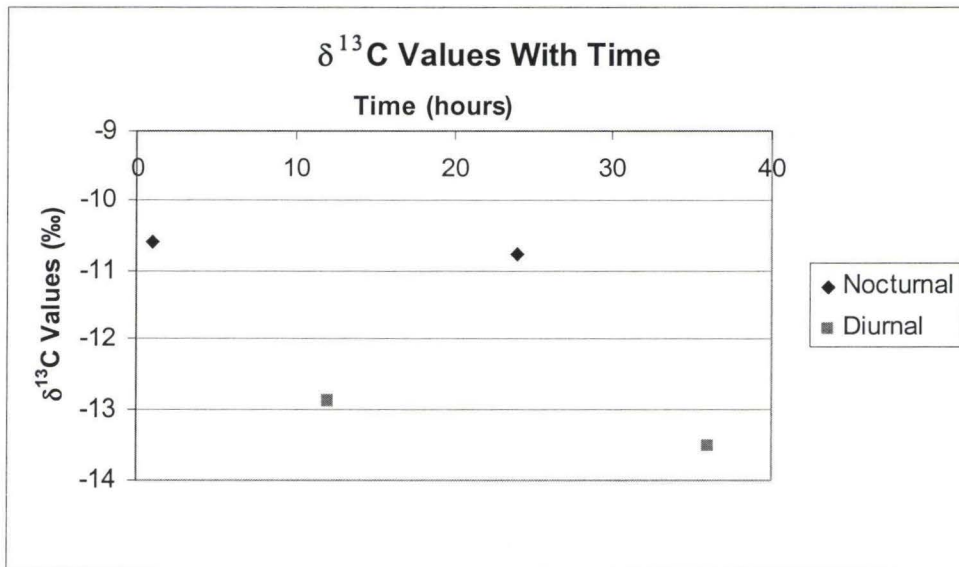


Figure 13. $\delta^{13}\text{C}$ values with time. Time starts at 5:50 p.m. January 7, 2003, and ends 6 p.m. January 9, 2003. Each point represents the average $\delta^{13}\text{C}$ value for approximately the next 12 hours (sunrise to sunset, or vice versa).

4.5 RECHARGE ZONE SOIL GAS $\delta^{13}\text{C}$ VALUES AND ECOSYSTEM CHANGE

$\delta^{13}\text{C}$ values in Area 1 translate to a $\delta^{13}\text{C}_{\text{DIC}}$ of -3‰ today, calculated from (Clark 1997):

$$(9) \delta^{13}\text{C}_{\text{DIC}} = m\text{HCO}_3^- (\delta^{13}\text{C}_{\text{soil gas}} + \epsilon_{\text{CO}_2\text{g-HCO}_3^-}) + m\text{CO}_2 (\text{aq}) (\delta^{13}\text{C}_{\text{soil gas}} + \epsilon_{\text{CO}_2\text{aq-CO}_2\text{g}})$$

Using a soil temperature of 12 °C (285 K), the pK_1 (6.438) and fractionation factors (9.267, -1.11) were found using (3), (7), and (8). This temperature is within the soil temperature range found for Laumaia soils in the Area 1 of this study (11-12 °C). Additionally, soil temperatures can be found from the graph of mean annual temperature with elevation and adding two degrees (Fahrenheit scale) (Niemeyer 2003). At the elevation of ~2100 m, the mean annual temperature is approximately 11 °C, with a soil temperature estimate of 12 °C. The year-round average soil gas $\delta^{13}\text{C}$ value of -12‰ (found in this study) for Area 1 was used as the $\delta^{13}\text{C}$ value of soil gas CO_2 in (9). The effect of temperature on this value is small; changing it by one K yields the same result.

From borehole waters, the $\delta^{13}\text{C}_{\text{DIC}}$ value 2200 years ago was -12‰, a difference of 9‰ from today's expected DIC. However, further correction of this value must be made. Approximately 2200 years ago, atmospheric $\delta^{13}\text{C}$ values were roughly 1.5‰ to 2‰ more enriched than today, due to the addition of light $\delta^{13}\text{C}$ values from the burning of fossil fuels occurring in recent times (Indermuhle 1999). Plants using atmospheric air then would have an average $\delta^{13}\text{C}_{\text{DIC}}$ value 2‰ heavier than plants using atmospheric air today. Therefore, all other factors being equal, the difference in the $\delta^{13}\text{C}_{\text{DIC}}$ values is actually 11‰. This shift in $\delta^{13}\text{C}_{\text{DIC}}$ value indicates a significant change in the $\delta^{13}\text{C}$ value of the source of the CO_2 in the past 2200 years. The $\delta^{13}\text{C}_{\text{DIC}}$ value corresponds to a soil gas $\delta^{13}\text{C}$ value of approximately -21‰ 2200 years ago (equivalent to -23‰ today, with current atmospheric air), indicative of a mainly C_3 ecosystem, whereas current $\delta^{13}\text{C}$ values of -12‰ are a result of mainly C_4 vegetation. Since the source of soil gas CO_2 is

CO₂ respired by the live root respiration from vegetation in the area (with a contribution from microbial respiration), the average of all $\delta^{13}\text{C}$ values in the pasture indicates that there has been an ecosystem change in that time. Given the historical records, the recharge area in this project 2200 years ago would have been a koa forest with fingers of ohia and mamani scattered throughout (Jeffrey 2003), with a soil gas $\delta^{13}\text{C}$ value typical of C₃ vegetation ($\sim -22\text{‰}$) (Boutton 1991a). This is consistent with the value calculated above. Trees are mainly C₃ species; therefore, this shift is consistent with our hypothesis that the ecosystem has changed (Quade 1995).

The transition from forest to pasture is considered to be a result of two major influences, both related to the arrival of humans on the island: conversion of forest to grazing areas for cows, horses, and other farm animals, and the intentional or accidental introduction of exotic grasses and wildlife by humans. Feral goats and pigs are prevalent on the island, destroying rainforest understories, promoting soil erosion, and drastically altering their ecosystem (Mueller-Dombois 1998). It is reported that while several grass taxa existed on the islands before human habitation (Polynesians arrived 300-400 A. D., Europeans in the late 1700's), the area of open grasslands increased tremendously with the intentional introduction of several invasive, noxious grass species. These grasses were brought to the islands for the specific purpose of providing favorable grazing material. The exotic grasses and animals have spread quickly over the islands, and previously unthreatened species have been choked out of some of their natural habitats, or eliminated completely. Many introduced plants and animals are highly adapted for

competition; in contrast, species that are native to the islands have evolved in a habitat where it was not necessary to vie for space or resources. As a result, some of the once endemic species have become extinct in the Hawaiian Islands (Mueller-Dombois 1998).

In terms of preservation and aesthetics, many efforts have been made to reverse the impact of these changes to Hawai'i's ecosystem. However, the environment also has an impact on the life of humans. The ramifications of ecosystem change are drastic: ecosystem conversion can affect precipitation patterns, drainage and erosion dynamics, and heat budgets on a local or regional scale (Meher-Homji 1989; Salati 1991; Ravindranath 1998). Large amounts of change worldwide could eventually have a global impact (Karl 1997; Kricher 1997). The greatest change is seen in the intensity of rainfall events. Even if the amount of rainfall does not change, deforestation tends to decrease the number and duration, but increase the intensity, of rainfall events. Erratic, torrential rainfall events could lead to devastating floods. This leads to larger amounts of runoff and erosion, and longer periods of dryness. Eventually, the long intervals of aridity allow small streams to dry up and dust to accumulate. If conditions worsen, desertification could eventually occur (Meher-Homji 1980a; Meher-Homji 1980b; Reynolds 1988).

On a local scale, the conversion of forest to pasture has been documented to alter rainfall distributions. Grasses do not allow any significant amount of rainfall capture, decreasing the amount of water that can evaporate. It is postulated that a decrease in evaporation could cause a decrease in rainfall. Cleared forest areas are often found to

have been more mesophytic than the same area, now occupied by pasture. This alone indicates the drying effect of forest conversion (Mueller-Dombois 1998).

Less rainfall in Hawai'i could have major consequences, as many people rely on above-ground rainfall catchments to supply their everyday water, and Hawai'i is far from any outside supply of water (Anthony 1993). With population increases, this could strain resources. If Hawai'i does start to rely solely on aquifers for water, smaller amounts of rainfall would have obvious negative impacts on this resource, as well (Bruijnzeel 1986; Ravindranath 1998).

In this study, the use of soil gas $\delta^{13}\text{C}$ values as a proxy for ecosystem change was contingent upon two key assumptions: 1) soil gas CO_2 was the main source of $\delta^{13}\text{C}$ values in the 2200 year old DIC, and 2) no change in the $\delta^{13}\text{C}$ value of the DIC occurred during the flow of the water through the aquifer due to outside chemical reactions (mainly methanogenesis, sulfate reduction, carbonate, or calcite dissolution/deposition). In the absence of limestone and other carbonate materials, the first assumption is met (Boutton 1991b). In the borehole waters and core, no evidence of anaerobic conditions, and no sulfate or sulfide, and very little calcite were found, eliminating the influence of these potentially $\delta^{13}\text{C}$ -altering reactions (Thomas 2004). Therefore, soil gas $\delta^{13}\text{C}$ values and $\delta^{13}\text{C}_{\text{DIC}}$ values in groundwater can be and are used in this study to indicate ecosystem change due to human or natural causes.

4.6 FUTURE WORK

This study can be used as a model for future studies using isotopes as proxies of ecosystem change. To further support this study, it would be helpful to perform a similar study on waters with different ^{14}C ages to learn if the $\delta^{13}\text{C}$ values show a consistent pattern through time. The current study could also be supported by examining the $\delta^{13}\text{C}$ values of DIC in waters where the ecosystem of the recharge zone is known and comparing them to the predicted $\delta^{13}\text{C}$ values for that ecosystem.

There are several ways this study could be expanded upon. A depth profile in the soil to determine what layer of soil horizon is responsible for the observed $\delta^{13}\text{C}$ values in the soil gas would elucidate why no correlation was found between $\delta^{13}\text{C}$ values and CO_2 concentrations with depth. An experiment separating the microbial and root respiration contributions could be performed by using a root and plant killing agent on a plot of earth, eliminating live root respiration. Soil gas samples could be taken from the bare patch of earth and compared to a vegetated area. Nocturnal and diurnal production of each of these sources could be quantified using this method, as well.

REFERENCES

- Allard, P., Carbonnelle, J., Dajlevic, D., Le Bronec, J., Morel, P., Robe, M. C., Maurenas, J. M., Faivre-Pierret, R., Martin, D., Sabroux, J. C., and Zettwoog, P. (1991). "Eruptive and diffuse emissions of CO₂ from Mount Etna." Nature **351**: 387-391.
- Amundson, R., Stern, Libby, Baisden, Troy, and Wang, Yang (1998). "The isotopic composition of soil and soil-respired CO₂." Geoderma **82**: 83-114.
- Andrews, J. A., Harrison, K. G., Matamalia, R., and Schlesinger, W. H. (1999). "Separation of root respiration from total soil respiration using carbon-13 labeling during Free-Air Carbon Dioxide Enrichment (FACE)." Soil Science Society of America Journal **63**(5): 1429-1435.
- Andrews, J. A., Harrison, Kevin G., Matamala, Roser, Schlesinger, William H. (1999). "Separation of root respiration from total soil respiration using carbon-13 labeling during Free-Air Carbon Dioxide Enrichment (FACE)." Soil Science Society of America Journal **63**: 1429-1435.
- Anthony, S., Mayer, William, Ewart, Charles J., and Shade, Patricia J. (1993). "Island Hydrology: Hawaii and Micronesia." Research and Exploration(Water Issue): 114-125.
- Appenzeller, T. (1992). "What drives climate?" Discover **November 1992**: 66-73.
- Barnola, J. M., Raynaud, D., Korotkevich, Y. S., and Lorius, C. (1987). "Vostok ice core provides 160,000-year record of atmospheric CO₂." Nature **329**: 408-414.
- Bolin, B., Degens, E. T., Kempe, S., and Ketner, P. (1979). The Global Biogeochemical Carbon Cycle. The Global Carbon Cycle. B. Bolin, Degens, E. T., Kempe, S., and Ketner, P. New York, New York, John Wiley and Sons. **13**: 1-56.
- Boutton, T. W. (1991a). Stable carbon isotope ratios of natural materials: II. Atmospheric, terrestrial, marine, and freshwater environments. Carbon Isotope Techniques. D. C. Coleman, and Fry, Brian. San Diego, CA, Academic Press, Inc. Harcourt Brace Jovanovich: 173-185.
- Boutton, T. W. (1991b). Stable carbon isotope ratios of natural materials: I. sample preparation and mass spectrometric analysis. Carbon Isotope Techniques. D. C. Coleman, and Fry, Brian. San Diego, CA, Academic Press, Inc. Harcourt Brace Jovanovich: 155-171.

- Box, E. O. (1988). "Estimating the seasonal carbon source-sink geography of a natural, steady-state terrestrial biosphere." Journal of Applied Meteorology **27**: 1109-1124.
- Bramryd, T. (1979). The effects of man on the biogeochemical cycle of carbon in terrestrial ecosystems. The Global Carbon Cycle. B. Bolin, Degens, E. T., Kempe, S., and Ketner, P. New York, NY, John Wiley and Sons. **13**: 183-218.
- Broadmeadow, M. S. J., Griffiths, H., Maxwell, C., and Borland, A. M. (1992). "The carbon isotope ratio of plant organic material reflects temporal and spatial variations in CO₂ within tropical forest formations in Trinidad." Oecologia **89**: 435-441.
- Bruijnzeel, P. S. (1986). "Environmental impacts of (de)forestation in the humid tropics-- A watershed perspective." Wallaceana **46**: 3-13.
- Buchmann, N., Guehl, J.-M., Barigah, T. S., Ehleringer, J.R. (1997a). "Interseasonal comparison of CO₂ concentrations, isotopic composition, and carbon dynamics in an Amazonian rainforest (French Guiana)." Oecologia **110**: 120-131.
- Buchmann, N., Kao, Wen-Yuan, and Ehleringer, Jim (1997b). "Influence of stand structure on carbon-13 of vegetation, soils, and canopy air within deciduous and evergreen forests in Utah, United States." Oecologia **110**: 109-119.
- Buyanovsky, G. A., and Wagner, G. H. (1983). "Annual cycles of carbon dioxide level in soil air." Soil Science Society of America Journal **47**: 1139-1145.
- Cabido, M., Ateca, Norma, Astegiano, Marta E., and Anton, Ana M. (1997). "Distribution of C₃ and C₄ grasses along an altitudinal gradient in Central Argentina." Journal of Biogeography **24**: 197-204.
- Cerling, T., E., Solomon, D. Kip, Quade, Jay, and Bowman, John R. (1991). "On the isotopic composition of carbon in soil carbon dioxide." Geochimica et Cosmochimica Acta **55**: 3403-3405.
- Cerling, T., Wang, Yang, and Quade, Jay (1993). "Expansion of C₄ ecosystems as an indicator of global ecological change in the late Miocene." Nature **361**: 344-345.
- Chapelle, F. H. (2000). "The significance of microbial processes in hydrogeology and geochemistry." Hydrogeology Journal **8**(1): 41-46.
- Chazdon, R. L. (1978). "Ecological aspects of the distribution of C₄ grasses in selected habitats of Costa Rica." Biotropica **10**(4): 265-269.

Clark, I. D., and Fritz, Peter (1997). Environmental isotopes in hydrogeology. New York, Lewis Publishers.

Clark, W. C., Cook, Kerry H., Marland, Gregg, Weinberg, Alvin M., Rotty, Ralph M., Bell, P. R., Allison, Linda J., and Cooper, Chester L. (1982). The Carbon Dioxide Question: Perspectives for 1982. Carbon Dioxide Review: 1982. W. C. Clark. New York, NY, Oxford University Press: 469.

Cole, D. R., and Monger, H. Curtis (1994). "Influence of atmospheric CO₂ on the decline of C₄ plants during the last deglaciation." Nature **368**: 533-536.

Collatz, G. J., Berry, Joseph A., Clark, James S. (1998). "Effects of climate and atmospheric CO₂ partial pressure on the global distribution of C₄ grasses: present, past, and future." Oecologia **114**: 441-454.

Davidson, E. A., Ackerman, I. L. (1993). "Changes in soil carbon inventories following cultivation of previously untilled soils." Biogeochemistry **20**: 161-193.

Davidson, G. R. (1995). "The stable isotopic composition and measurement of carbon in soil CO₂." Geochimica et Cosmochimica Acta **59**(12): 2485-2489.

Dorr, H., and Munnich, Karl Otto (1980). "Carbon-14 and carbon-13 in soil CO₂." Radiocarbon **22**(3): 909-918.

Dudziak, A., and Halas, Stanislaw (1996). "Diurnal cycle of carbon isotope ratio in soil CO₂ in various ecosystems." Plant and Soil **183**: 291-299.

Edwards, N. T. (1975). "Effects of temperature and moisture on carbon dioxide evolution in a mixed deciduous forest floor." Soil Science Society of America Proceedings **39**: 361-365.

Ehleringer, J. R., and Monson, Russell K. (1993). "Evolutionary and ecological aspects of photosynthetic pathway variation." Annual Review of Ecological Systems **24**: 411-439.

Ehleringer, J. R., Cerling, Thure E., and Helliker, Brent R. (1997). "C₄ photosynthesis, atmospheric CO₂, and climate." Oecologia **112**: 285-299.

Ekblad, A., and Hogberg, Peter (2000). "Analysis of $\delta^{13}\text{C}$ of CO₂ distinguishes between microbial respiration of added C₄-sucrose and other soil respiration in a C₃-ecosystem." Plant and Soil **219**: 197-209.

- Felske, A., Wolterink, Arthur, Van Lis, Robert, De Vos, Willem M., and Akkermans, Antoon D. L. (2000). "Response to soil bacterial community to grassland succession as monitored by 16S rRNA levels of the predominant ribotypes." Applied and Environmental Microbiology **66**(9): 3998-4003.
- Finlayson, J. B. (1992). "A soil gas survey over rotorua geothermal field, Rotorua, New Zealand." Geothermics **21**(1-2): 181-195.
- Francey, R. J., Tans, P. P., Allison, C. E., Enting, I. G., White, J. W. C., and Trolier, M. (1995). "Changes in oceanic and terrestrial carbon uptake since 1982." Nature **373**: 326-330.
- Freckman, D. W. (1994). *Life in the Soil. Soil biodiversity: its importance to ecosystem processes.* London, England, Natural History Museum: 26 pgs.
- Freckman, D. W. (1994). *Life in the Soil--Soil biodiversity: its importance to ecosystem processes.* London, England, Natural History Museum: 26.
- Freijer, J. I., and Leffelaar, P. A. (1996). "Adapted Fick's law applied to soil respiration." Water Resources Research **32**(4): 791-800.
- Freyer, H.-D. (1979). Atmospheric cycles of trace gases containing carbon. The Global Carbon Cycle. B. Bolin, Degens, E. T., Kempe, S., and Ketner, P. New York, NY, John Wiley and Sons. **13**: 101-128.
- Freyer, H.-D. (1979). Variations in the atmospheric CO₂ content. The Global Carbon Cycle. B. Bolin, Degens, E. T., Kempe, S., and Ketner, P. New York, NY, John Wiley and Sons. **13**: 79-99.
- Frimmel, F. H. (1998). "Characterization of natural organic matter as major constituents in aquatic systems." Journal of Contaminant Hydrology **35**(1-3): 201-216.
- Fry, B., and Sherr, E. B. (1989). $\delta^{13}\text{C}$ measurements as indicators of carbon flow in marine and freshwater ecosystems. Stable Isotopes in Ecological Research. P. W. Rundel, Ehleringer, J. R., and Nagy, K. A. New York, NY, Springer-Verlag. **68**: 196-229.
- Gaudinski, J. B., Trumbore, Susan E., Davidson, Eric A., and Zheng, Shuhui (2000). "Soil carbon cycling in a temperate forest: radiocarbon-based estimates of residence times, sequestration rates and partitioning of fluxes." Biogeochemistry **51**: 33-69.

- Gerlach, T. M., and Taylor, Bruce E. (1990). "Carbon isotope constraints on degassing of carbon dioxide from Kilauea Volcano." Geochimica et Cosmochimica Acta **54**: 2051-2088.
- Gerlach, T. M., and Thomas, Donald M. (1986). "Carbon and sulphur isotopic composition of Kilauea parental magma." Nature **319**: 480-482.
- Giambelluca, T. W., Nullet, Michael A., and Schroeder, Thomas A. (1986). Rainfall Atlas of Hawaii. Honolulu, HI, Water Resources Research Center and Department of Meteorology, University of Hawaii at Manoa: 276.
- Giardina, C. P., and Ryan, M. G. (2000). "Evidence that temperature does not influence the decomposition of organic carbon in forest mineral soils." Nature **404**: 858-861.
- Hackl, E., Bachmann, G., and Zechmeister-Boltenstern, S. (2000). "Soil microbial biomass and rhizosphere effects in natural forest stands." Phyton **40**: 93-90.
- Hanson, P. J., Edwards, N. T., Garten, C. T., and Andrews, J. A. (2000). "Separating root and soil microbial contributions to soil respiration: A review of methods and observations." Biogeochemistry **48**: 115-146.
- Hanson, P. J., Edwards, N. T., Garten, C. T., Andrews, J. A. (2000). "Separating root and soil microbial contributions to soil respiration: a review of methods and observations." Biogeochemistry **48**(1): 115-146.
- Hattersley, P. W. (1983). "The distribution of C₃ and C₄ grasses in Australia in relation to climate." Oecologia **57**: 113-128.
- Hayes, J. M. (2001). Fractionation of the Isotopes of Carbon and Hydrogen in Biosynthetic processes. National Meeting of the Geological Society of America, Boston, MA, Mineralogical Society of America.
- Hendry, M. J., Lawrence, J. R., Zanyk, B. N., and Kirkland, R. (1993). "Microbial production of CO₂ in unsaturated geologic media in a mesoscale model." Water Resources Research **29**(4): 973-984.
- Henn, M., and Chapela, Ignacio H. (2000). "Differential C isotope discrimination by fungi during decomposition of C₃- and C₄-derived sucrose." Applied and Environmental Microbiology **66**(10): 4180-4186.

Hesterberg, R., and Siegenthaler, Ulrich (1991). "Production and stable isotopic composition of CO₂ in a soil near Bern, Switzerland." Tellus **43B**: 197-205.

Huang, B., and Liu, Xiaozhong (2003). "Summer Root Decline: Production and Mortality for Four Cultivars of Creeping Bentgrass." Crop Science **43**(258-265).

Huck, M. G., Hageman, R. H., Hanson, J. B. (1962). "Diurnal variation in root respiration." Plant Physiology **37**: 371-375.

Hufen, T. H., Lau, L. S., and Buddemeier, R. W. (1974). Radiocarbon, carbon-13 and tritium in water samples from basaltic aquifers and carbonate aquifers on the Island of Oahu, Hawaii. IAEA Proceedings Symposium, Vienna, Austria, International Atomic Energy Agency.

Indermuhle, A., Stocker, T.F., Joos, F., Fischer, H., Smith, H.J., Wahlen, M., Deck, B., Mastroianni, D., Tschumi, J., Blunier, T., Meyer, R. and Stauffer, B. (1999). "Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica." Nature **398**: 121-126.

Javoy, M., Pineau, F., and Delorme, H. (1986). "Carbon and nitrogen isotopes in the mantle." Chemical Geology **57**: 41-62.

Jeffrey, J. (2003). Vegetation on Mauna Kea 2200 years ago.

Karl, T. R. N., N. & Gregory, J. (1997). "The Coming Climate." Scientific American **269**(5): 78-83.

Kasting, J. F. (1998). "The Carbon Cycle, Climate, and the Long-Term Effects of Fossil Fuel Burning." Consequences **4**(1).

Keeling, C. D., Bacastow, Robert B., Whorf, Timothy P. (1982). Measurements of the concentration of carbon dioxide at Mauna Loa Observatory, Hawaii. Carbon Dioxide Review: 1982. W. C. Clark. New York, NY, Oxford University Press: 469.

Keeling, C. D. a. W., T. P. (2002). Atmospheric CO₂ records from sites in the SIO air sampling network. Trends: A Compendium of Data on Global Change. Oak Ridge, TN, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy.

Kendall, C. a. J. J. M., Ed. (1998). Isotope Tracers in Catchment Hydrology. Amsterdam, Elsevier Science, B. V.

Kerr, R. (1992). "Fugitive carbon dioxide: It's not hiding in the ocean." Science **256**(3 April 1992): 35.

Kricher, J. (1997). A Neotropical Companion. Princeton, NJ, Princeton University Press.

Kuypers, M. M. M., Pancost, Richard D., and Damste, Jaap S. Sinninghe (1999). "A large and abrupt fall in atmospheric CO₂ concentration during Cretaceous times." Nature **399**: 342-345.

Kuzyakov, Y., Cheng, W. (2001). "Photosynthesis controls of rhizosphere respiration and organic matter composition." Soil Biology and Biochemistry **33**: 1915-1925.

Lee-Thorpe, J. a. B., Peter B. (1990). "Environmental shifts in the last 20,000 years: isotopic evidence from Equus Cave." South African Journal of Science **86**: 452-453.

Lewis, E., and D. W. R. Wallace (1998). ORNL/CDIAC-105. Program Developed for CO₂ System. Calculations. Oak Ridge, Tennessee, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy.

Manahan, S. E. (2000). Environmental Chemistry. New York, NY, Lewis Publishers.

Mary, B., Mariotti, A., Morel, J. L. (1992). "Use of ¹³C at natural abundance for studying the biodegradation of root mucilage, roots and glucose in soil." Soil Biology and Biochemistry **24**(10): 1065-1072.

Mathews, B. (2003). C₃ and C₄ grasses on the Big Island. E. Smid. Hilo, HI.

McIntosh, J. C., Lynn M. Walter and Anna M. Martini. 2004: Extensive microbial modification of formation water geochemistry: Case study from a Midcontinent sedimentary basin, United States. Geological Society of America Bulletin: Vol. 116, No. 5, pp. 743–759. (2004). "Extensive microbial modification of formation water geochemistry: Case study from a Midcontinent sedimentary basin, United States." Geological Society of America Bulletin **116**(5): 743–759.

Meher-Homji, V. M. (1980a). "The link between rainfall and forest clearance: Case studies from Western Karnataka." Transaction of the Institute of Indian Geographers **2**(1): 59-65.

Meher-Homji, V. M. (1980b). "Repercussions of deforestation on precipitation in Western Karnataka, India." Archiv. für Meteorol. Geophys. Bioklimat. **28B**: 385-400.

Meher-Homji, V. M. (1989). Trends in rainfall in relation to forest cover. Deforestation, drought, and desertification: perceptions on a growing ecological crisis. N. D. Jayal. New Delhi, Indian National Trust for Art and Cultural Heritage.

Mook, W. G., Ed. (2001). UNESCO/IAEA Series on Environmental Isotopes in the Hydrological Cycle: Principles and Applications, UNESCO/IAEA.

Mueller-Dombois, D., and Fosberg, F. Ray (1998). Vegetation of the Tropical Pacific Islands. New York, NY, Springer.

Niemeyer, P. (2003). Mauna Kea soil temperatures. E. Smid. Honolulu, HI.

NOAA Climate Monitoring and Diagnostics Laboratory, C. C. G. G. (2004). Interactive Atmospheric Data Visualization.

NOAA, P. R. H. (2004). National Weather Service Forecast Office.

Nullet, D., Ikawa, Haruyoshi, and Kilham, Phoebe (1990). "Local differences in soil temperature and soil moisture regimes on a mountain slope, Hawaii." Geoderma **47**: 171-184.

O'Leary, M. H. (1981). "Carbon isotope fractionation in plants." Phytochemistry **20**(4): 553-567.

O'Leary, M. H. (1988). "Carbon isotopes in photosynthesis." BioScience **38**(5): 328-335.

Paull, C. K., Lorenson, T. D., Borowski, W. S., Ussler III, W., Olsen, K., and Rodriguez, N. M. (2000). Isotopic composition of CH₄, CO₂ species, and sedimentary organic matter within samples from the Blake Ridge: gas source implications. Proceedings of ODP, Scientific Results. C. K. Paull, Matsumoto, R., Wallace, P. J., and Dillon, W. P. College Station, TX, Ocean Drilling Program. **164**: 67-78.

Pettersson, C., Ephraim J., and Allard B. (1994). "On the composition and properties of humic substances isolated from deep groundwater and surface waters." Organic Geochemistry **21**(5): 443-451.

Puckett, L. J., Cowdery, Timothy K. (2002). "Transport and Fate of Nitrate in a Glacial Outwash Aquifer in Relation to Ground Water Age, Land Use Practices, and Redox Processes." Journal of Environmental Quality **31**: 782-796.

- Quade, J., and Cerling, Thure E. (1995). "Expansion of C₄ grasses in the Late Miocene of Northern Pakistan: evidence from stable isotopes in paleosols." Palaeogeography, Palaeoclimatology, Palaeoecology **15**: 91-116.
- Raich, J. W., and Schlesinger, W. H. (1992). "The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate." Tellus **44B**: 81-99.
- Ravindranath, N. H., and Sukumar, R. (1998). "Climate change and tropical forests in India." Climatic Change **39**: 563-581.
- Reynolds, E. R. C., and Thompson, Frank B., Ed. (1988). Forests, Climate, and Hydrology. Singapore, Kefford Press.
- Ruddiman, W. F. (2001). Earth's Climate Past and Future. New York, NY, W. H. Freeman and Company.
- Rundel, P. W. (1980). "The ecological distribution of C₄ and C₃ grasses in the Hawaiian Islands." Oecologia **45**: 345-359.
- Rustad, L., Huntington, Thomas G., and Boone, Richard D. (2000). "Controls on soil respiration: Implications for climate change." Biogeochemistry **48**: 1-6.
- Salati, E., and Nobre, Carlos A. (1991). "Possible climatic impacts of tropical deforestation." Climatic Change **19**: 177-196.
- Sanderson, M., Ed. (1993). Prevailing Trade Winds; Climate and Weather in Hawaii. Honolulu, HI, University of Hawaii Press.
- Sato, H. H., Ikeda, Warren, Paeth, Robert, Smythe, Richard, and Takehiro Jr., Minoru (1973). Soil Survey of the Island of Hawaii, State of Hawaii. Washington, D.C., U.S. Department of Agriculture, Soil Conservation Service, with the University of Hawaii Agricultural Experiment Station: 115.
- Schlesinger, W. H., Winkler, Julia Palmer, and Megonigal, J. Patrick (2000). Soils and the Global Carbon Cycle. The Carbon Cycle. T. M. L. Wigley, and Schimel, D. S. New York, NY, Cambridge University Press: 93-101.
- Schubler, W., Neubert, Rolf, Levin, Ingeborg, and Fischer, Natalie (2000). "Determination of microbial versus root-produced CO₂ in an agricultural ecosystem by means of $\delta^{13}\text{C}$ measurements in soil air." Tellus **52B**: 909-918.

Sternberg, L. S. L., Mulkey, Stephen, and Wright, S. Joseph (1989). "Ecological interpretation of leaf carbon isotope ratios: influence of respired carbon dioxide." Ecology **70**(5): 1317-1324.

Stevenson, F. J., and Cole, M. A. (1999). Cycles of Soil, Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients. New York, New York, John Wiley & Sons, Inc.

Thomas, D. (2004). Borehole water conditions.

Thomas, D. M., Paillet, F. L., and Conrad, M. E. (1996). "Hydrogeology of the Hawaii Scientific Drilling Project borehole KP-1 2. Groundwater geochemistry and regional flow patterns." Journal of Geophysical Research **101**(B5): 11683-11694.

Tieszen, L. L., Senyimba, Michael M., Imbamba, Simeon K., Troughton, John H. (1979). "The distribution of C₃ and C₄ grasses and carbon isotope discrimination along an altitudinal and moisture gradient in Kenya." Oecologia **37**: 337-350.

Townsend, A. R., Vitousek, Peter M., and Trumbore, Susan E. (1995). "Soil organic matter dynamics along gradients in temperature and land use on the island of Hawaii." Ecology **76**(3): 721-733.

Townsend, A. R., Vitousek, Peter M., Desmarais, David J., and Tharpe, Anne (1997). "Soil carbon pool structure and temperature sensitivity inferred using CO₂ and ¹³CO₂ incubation fluxes from five Hawaiian soils." Biogeochemistry **38**: 1-17.

Voss, C. I., and Wood, W. W. (1994). Synthesis of geochemical isotopic and groundwater modeling analysis to explain regional flow in a coastal aquifer of southern Oahu, Hawaii. Mathematical models and their applications to isotope studies in groundwater hydrology. Vienna, International Atomic Energy Agency (IAEA).

Witkamp, M. (1969). "Cycles of temperature and carbon dioxide evolution from litter and soil." Ecology **50**(5): 922-924.

Wofsy, S. C. (2001). "Where has all the carbon gone?" Science **292**(22June 2001): 2261-2263.

Wolfe, E. W., Wise, William S., and Dalrymple, G. Brent (1997). The Geology and Petrology of Mauna Kea Volcano, Hawaii--A study of postshield Volcanism. Menlo Park, CA, U. S. Geological Survey: 129.

Wood, W. W., and Petraitis, Michael J. (1984). "Origin and distribution of carbon dioxide in the unsaturated zone of the southern high plains of Texas." Water Resources Research **20**(9): 1193-1208.

Yamaguchi, M., Flocker, W. J., and Howard, F.D. (1967). "Soil Atmosphere as influenced by temperature and moisture." Soil Science Society of America Proceedings **31**: 164-167.

Zabkiewicz, J. A., Gaskin, R. E. (1978). Effect of fire on gorse seeds. Proceedings of the 31st New Zealand Weed and Pest Control Conference: 47-52.

Zeebe, R. E., and Wolf-Gladrow, Dieter (2001). CO₂ in seawater: Equilibrium, Kinetics, Isotopes. New York, NY, Elsevier.

98 141HI 3560
04/09 TH 21280-6
EIT Group